PERFLUOROPINACOL DERIVATIVES OF GROUP V AND VII

A STUDY OF THE NATURE OF PERFLUOROALKYL VICINAL DIHYPOCHLORITE AND THE REACTION OF DISODIUM PERFLUOROPINACOLATE WITH GROUP V COMPOUNDS

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ABSTRACT

The reaction of perfluoroalkyl vicinal dihypochlorite with carbon monoxide, sulphur dioxide, benzaldehyde and tri henyl phosphine is described and the reaction products we e characterized by infrared and n. m. r. spectroscopy.

Group V derivatives of perfluoropinacol were prepared the reaction of disodium perfluoropinacolate with triphenyl hosphorus dibromide, triphenyl arsenic dichloride, triphenyl antimony dichloride and phenyl arsenic dichloride. The products were characterized by fluorine n. m. r., infrared spectroscopy and mass spectrometry.

Some reactions of chloroform with hexafluoroacetone and pentafluorochloroacetone were briefly investigated.

ACKNOWLEDGEMENTS

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GENERAL INTRODUCTION

Schutzenberger[1] in 1878 reported that acetyl hypochlorites could be formed by the action of chlorine monoxide on acetic acid.

$$Cl_2O + RCOOH \longrightarrow RCOOCl + H_2O$$

These acetyl hypochlorites can also be formed when chlorine is mixed with silver carboxylate in molecular proportions at low temperature[2].

$$RCOOAg + Cl_2 \longrightarrow RCOOCl + AgCl$$

These acetyl hypochlorites are rather unstable. They decompose readily to give the chloride and carbon dioxide when warmed slightly.

$$RCOOCl \longrightarrow RCl + CO_2$$

The first known alkyl hypochlorite was isolated in 1885 by Sandmeyer[3]. He obtained ethyl hypochlorite by the action of chlorine gas on ethyl alcohol in the cold.

$$C_2H_5OH + Cl_2 \longrightarrow C_2H_5OCl + HCl$$

His work was then studied by Chattaway[4] and Backeberg[5]. They were unable to obtain a pure sample of the hypochlorite above 0^{o} because it decomposed to aldehyde and hydrogen chloride.

$$C_2H_5OCl \longrightarrow CH_3CHO + HCl$$

Chattaway postulated the existence of other unstable hypochlorites[4] such as benzyl, propyl, butyl and amyl hypochlorites. It was shown that the order of stability of these compounds was:

tertiary > secondary > primary

The alkyl hypochlorites were found to be mobile, volatile liquids of strongirritating odour. The primary and secondary hypochlorites decomposed explosively to aldehydes or ketones respectively when exposed to light. Even in the dark, when they were heated to room temperature, decomposition occurred with the evolution of heat. The tertiary hypochlorites were more stable. They could be kept in the dark for a long period without signs of decomposition. However, when exposed to light or with the application of slight heating, they decomposed to ketone and alkyl chloride. The decomposition schemes were:

$$RCH_2OCl \longrightarrow RCHO + HCl$$

$$R_2CHOCl \longrightarrow R_2CO + HCl$$

$$R_3COCl \longrightarrow R_2CO + RCl$$

Other research workers[6,7] also postulated the existence of hypochlorites in oxidation reactions of alcohols.

The tertiary butyl hypochlorite has been extensively studied[8,3] due to its reasonable stability and ease of handling. It can be prepared by a number of methods, one of which is by passing chlorine through an alkaline solution of tertiary butanol at 0^{o} with the exclusion of light.

$$(CH_3)_3COH + Cl_2 + NaOH \longrightarrow (CH_3)_3COCl + NaCl + H_2O$$

Its reaction with organic compounds was studied extensively by Ginsberg[9,10]. He investigated the action of the tertiary butyl hypochlorite on a number of aromatic aldehydes which were finally oxidized to aromatic acids. The presence of the products provide a useful way of identifying hypochlorites.

$$RCHO + (CH_3)_3COCl \longrightarrow RCOCl + (CH_3)_3COH$$

$$RCOCl + (CH_3)_3COH \longrightarrow RCOOH + (CH_3)_3CCl$$

$$2C_6H_5CHO + (CH_3)_3COCl \longrightarrow C_6H_5COCl + C_6H_5COOH$$

The chlorination process has been shown to occur through a free radical mechanism catalysed by ultraviolet

radiation. However, such reactions can also be catalysed by a free radical initiator such as AIBN (azobisisobutylonitrile)[11].

Tertiary butyl hypochlorite has been shown to chlorinate phenols, ketones, hydrocarbons and alcohols. Unfortunately the yields are often only moderate and numerous isomers are produced due to uncontrolled chlorination.

An early hypofluorite was obtained by fluorination of carbon monoxide, carbonyl fluoride or methanol over a silver catalyst at 160 - 180° [12].

$$CO + 2F_2 \longrightarrow CF_3OF$$

Several other monofluoroxy derivatives[13] have been prepared by the direct action of fluorine with the corresponding partially fluorinated alcohol.

Perfluoro organic hypofluorite derivatives[14] can be prepared in a pure form by the reaction of fluorine with perfluoro-ketones in the presence of a metal fluoride.

$$\begin{matrix} X \\ Y \end{matrix}\!\!>C=O + F_2 \xrightarrow{MF} \begin{matrix} X \\ Y \end{matrix}\!\!>CFOF$$

$X = R_f$ or F, $Y = R_f$ or F, M = K, Rb or Cs.

Geminal bisfluoroxy compounds[15] were first reported by the fluorination of hexafluoroacetone hydrate or the monosodium salt of hexafluoroacetone to give hypofluorites.

$$(CF_3)_2C\lessdot^{OH}_{OH} + F_2 \longrightarrow (CF_3)_2CFOF + H_2O$$

$$(CF_3)_2C\lessdot^{OH}_{ONa} + F_2 \longrightarrow (CF_3)_2C\lessdot^{OF}_{OF} + NaF + HF$$

Fox[16] et al. recently have synthesized the first perfluoroalkyl hypochlorites R_fOCl. These compounds were prepared by the metal fluoride (CsF) catalysed reaction of perfluoroalkyl carbonyl compounds with chlorine monofluoride at -20°C.

$$\begin{matrix} R_{f1} \\ R_{f2} \end{matrix}\!\!>C=O + ClF \xrightarrow{CsF} \begin{matrix} R_{f1} \\ R_{f2} \end{matrix}\!\!>CFOCl$$

1. $R_{f1} = R_{f2} = F$
2. $R_{f1} = R_{f2} = CF_3$
3. $R_{f1} = CF_3$, $R_{f2} = F$

The reported compounds appear much more stable than the corresponding alkyl hypochlorites but decompose when stored at elevated temperatures.

Schack and Maya[17] also reported a similar preparation of the perfluoroalkyl hypochlorites.

$$(R_f)_2C=O + ClF \xrightarrow{MF} (R_f)_2CFOCl$$

$R_f = CF_3$ or F, M = K, Rb or Cs

These reactions occured in high yield (over 90%) in a few hours. The hypochlorites prepared in this manner were CF_3OCl, C_2F_5OCl and $(CF_3)_2CFOCl$. They found that the thermal stability of the compounds was in the order,

$$CF_3OCl > C_2F_5OCl > (CF_3)_2CFOCl$$

Since all of the hypochlorite syntheses involved addition of the elements of chlorine monofluoride across a carbonyl double bond, they were necessarily restricted to primary and secondary alkyl hypochlorites containing fluorine on the carbon atom bearing the -OCl function (i.e. α fluorine).

In an effort to extend the fluoroalkyl hypochlorite studies to include new members containing no α fluorine, Fox[18] et al. had examined the reactions of polyfluoroalcohols with chlorine monofluoride. These reactions proceeded smoothly to the desired hypochlorites according to the following equation at room temperature.

$$ROH + ClF \longrightarrow ROCl + HF$$

$$R = (CF_3)_3C,\ (CF_3)_2CH,\ CH_3C(CF_3)_2 \text{ or } CF_3CH_2$$

These hypochlorites, together with their perfluorinated predecessors, readily insert carbon monoxide and sulphur dioxide into the O-Cl bond to produce chloroformates and

chlorosulphates. The reactions were carried out routinely at -20°C.

$$ROCl + CO \longrightarrow ROC(O)Cl$$

$$ROCl + SO_2 \longrightarrow ROSO_2Cl$$

R = $(CF_3)_3C$, $(CF_3)_2CH$, $CH_3C(CF_3)_2$ or CF_3CH_2

However, when the same method was used to prepare perfluoroalkyl vicinal dihypochlorite, $(CF_3)_2C(OCl)C(CF_3)_2OCl$, from perfluoropinacol, $(CF_3)_2C(OH)C(CF_3)_2COH$, the only products found were those of degradation, namely, $(CF_3)_2CO$, $CF_3C(O)F$, F_2CO and CF_3Cl.

In the same year, nonetheless, Janzen and Pollitt[19] successfully prepared the perfluoroalkyl vicinal dihypochlorite. They also reported the synthesis of the bromide and iodide of the same family.

The hypochlorite and hypobromite were prepared by the reaction of disodium perfluoropinacolate with chlorine and bromine respectively. Attempts to extend the reaction to iodine were unsuccessful. The hypoiodite was prepared by reaction of disodium perfluoropinacolate with iodine monochloride or iodine monobromide. The reactions were conveniently carried out in the solvent trichlorofluoromethane at low temperature.

$$\begin{matrix}(CF_3)_2C\text{-}ONa \\ | \\ (CF_3)_2C\text{-}ONa\end{matrix} + 2\,X_2 \longrightarrow \begin{matrix}(CF_3)_2C\text{-}OX \\ | \\ (CF_3)_2C\text{-}OX\end{matrix} + 2\,NaX$$

1. X = Cl

2. X = Br

$$\begin{matrix}(CF_3)_2C\text{-}ONa \\ | \\ (CF_3)_2C\text{-}ONa\end{matrix} + 2\,IX \longrightarrow \begin{matrix}(CF_3)_2C\text{-}OI \\ | \\ (CF_3)_2C\text{-}OI\end{matrix} + 2\,NaX$$

X = Cl or Br

The stability of dihypohalites was briefly investigated. They were found to be stable at $0^{\circ}C$ in trichlorofluoromethane solution but decomposition occurred on standing at 25°. The rate of decomposition increased on heating or in the presence of ultraviolet light. Decomposition accompanied attempts to remove the last traces of solvent at reduced pressure in the vacuum system at room temperature. The hypochlorite and hypobromite were found to decompose if excess chlorine or bromine were used during the course of preparation.

Hexafluoroacetone, $(CF_3)_2CO$, was first prepared in 1941 and became commercially available in 1962. The reactions of hexafluoroacetone with various organic compounds have been studied in some detail, and the effect of fluorine subsitution has been to alter significantly the reactivity and the course of reaction. A review by Krespan and Middleton[20] summarizes the spectroscopy, properties, photolysis and reactions of hexafluoroacetone.

The reaction of the anhydrous metal fluorides with various fluorinated carbonyl compounds, for example, hexafluoroacetone, in donor solvent may lead to the preparation of ionic, fully fluorinated alkoxides of the heavier alkali metals. Trifluoromethoxides were produced by carbonyl fluoride while ethoxides and propoxides were produced by trifluoroacetyl fluoride[21], heptafluoropropionyl fluoride or hexafluoroacetone[22].

$$R_fCOF + MF \rightleftharpoons M^+(R_fCF_2O^-)$$

$$(CF_3)_2CO + MF \rightleftharpoons M^+((CF_3)_2CFO^-)$$

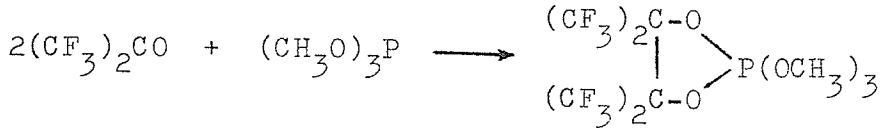
R_f = F, CF_3 or C_2F_5 M = K, Rb or Cs

For this type of ion, there must always be at least one fluorine atom attached to the α-carbon atom. As a result, the alkoxide and the carbonyl compound are in equilibrium.

The perfluoropinacol[23,24] was prepared via a triethyl phosphite intermediate. The latter was formed in high yield on merely mixing the two reactants.

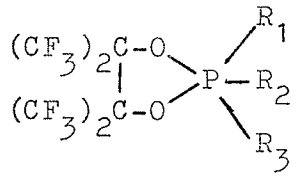
$$2(CF_3)_2CO + (C_2H_5O)_3P \longrightarrow \begin{matrix}(CF_3)_2C\text{-}O \\ | \quad \diagdown P(OEt)_3 \\ (CF_3)_2C\text{-}O \end{matrix} \xrightarrow{H_2SO_4} \begin{matrix}(CF_3)_2C\text{-}OH \\ | \\ (CF_3)_2C\text{-}OH \end{matrix}$$

Other such reactions between hexafluoroacetone and phosphites were also reported[25].



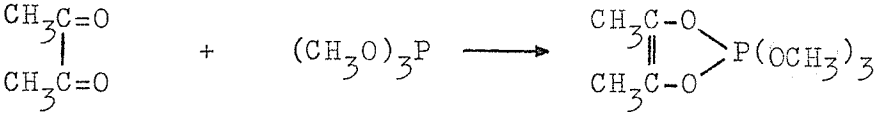
Reaction of hexafluoroacetone with triphenylphosphine was reported to give a phosphorane, which on hydrolysis liberated the perfluoropinacol[26].

Other recently synthesized phosphoranes[27,28] were,

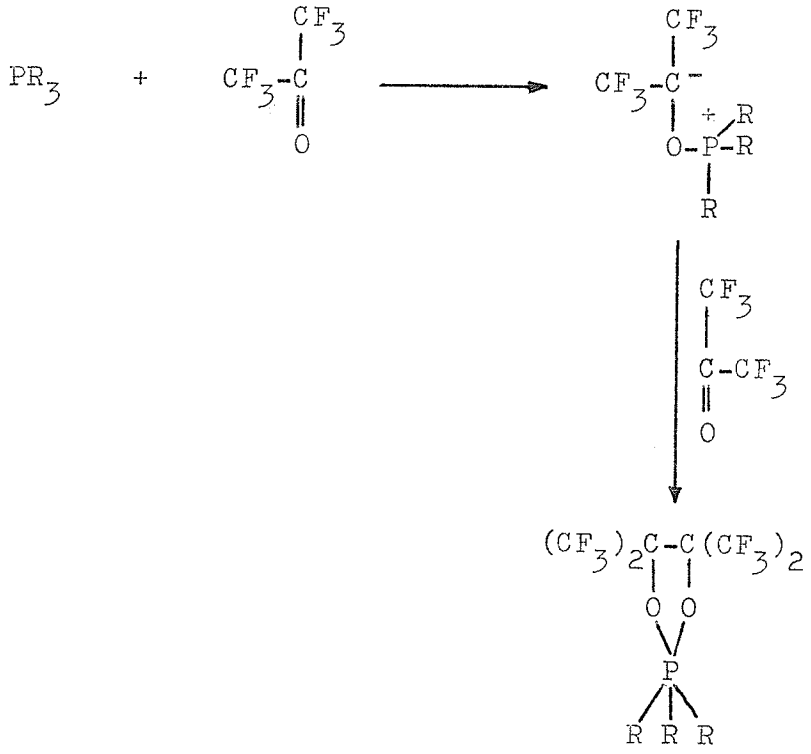


1. $R_1 = R_2 = R_3 = CH_3$
2. $R_1 = R_2 = R_3 = C_2H_5$
3. $R_1 = R_2 = C_2H_5$, $R_3 = C_6H_5$
4. $R_1 = R_2 = C_6H_5$, $R_3 = C_2H_5$

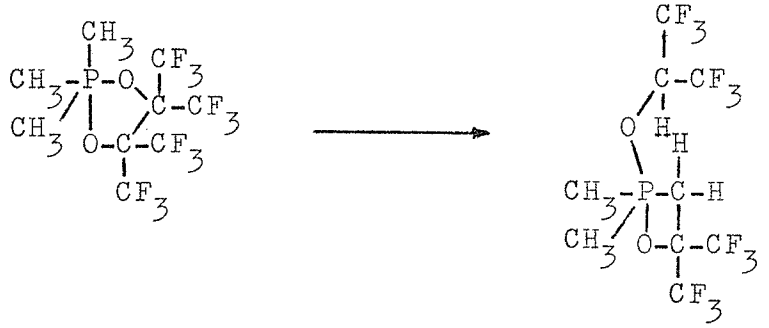
The non-fluorinated five-membered ringed phosphoranes can be prepared from phosphites and diketones[25].



It was suggested[29] that such kind of five-membered-ringed phosphoranes were formed from intermediate 1 : 1 adducts, resulting from the addition of trivalent phosphorus to carbonyl oxygen.



It was discovered[30] that these five-membered cyclic phosphoranes can be rearranged into four-membered cyclic phosphoranes, and the latter can be pyrolysed to olefins and phosphinate esters. One example of rearrangement is,



The reaction took place in benzene solution at 80°. In the rearrangement, a C-C bond was broken, a new C-C bond was formed, and a hydrogen atom was transferred from one carbon to another.

The four-membered cyclic phosphorane has the phosphorus at the center of a trigonal bipyramid, and the ring in an equatorial plane. Four possible diastereomers are assigned, two of them are meso and the others are racemic forms.

The organometallic chemists[31,32] have reported the synthesis of disodium or dilithium perfluoropinacolate. This was done by the reaction of sodium or lithium metal on hexafluoroacetone in a donor solvent such as tetrahydrofuran or glyme. The mechanism is an example of dimerization of a radical anion or ketyl postulated as an intermediate.

$$(CF_3)_2CO + Na \xrightarrow{\text{solvent}} (CF_3)_2CO^-Na^+$$

$$2\ (CF_3)_2CO^- \longrightarrow {}^-OC(CF_3)_2C(CF_3)_2O^-$$

Strong support for such a mechanism was reported by Janzen and Gerlock[33]. They made the hexafluoroacetone ketyl by the electrolytic reduction of hexafluoroacetone in acetonitrile.

$$CF_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}CF_3 + e \longrightarrow CF_3\text{-}\overset{\overset{O^-}{|}}{\dot{C}}\text{-}CF_3$$

The electron spin resonance of the dilute ketyl solution in acetonitrile gave a spectrum of seven groups of lines separated by about 35 gauss.

The disodium salt in solution provides a very convenient route to synthesize a number of alkoxides and esters of perfluoropinacol[34] and, especially, to prepare the cyclic derivatives.

The reaction of trimethychlorosilane with the solution gave immediate reaction to precipitate sodium chloride and the linear silicon derivative.

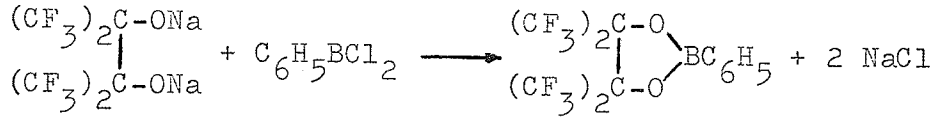
$$\begin{matrix}(CF_3)_2C\text{-}ONa\\ |\\ (CF_3)_2C\text{-}ONa\end{matrix} + 2\,(CH_3)_3SiCl \longrightarrow \begin{matrix}(CF_3)_2C\text{-}OSi(CH_3)_3\\ |\\ (CF_3)_2C\text{-}OSi(CH_3)_3\end{matrix} + 2NaCl$$

With dimethyl dichlorosilane, germane or stannane, the disodium alkoxide reacts to give the cyclic compounds.

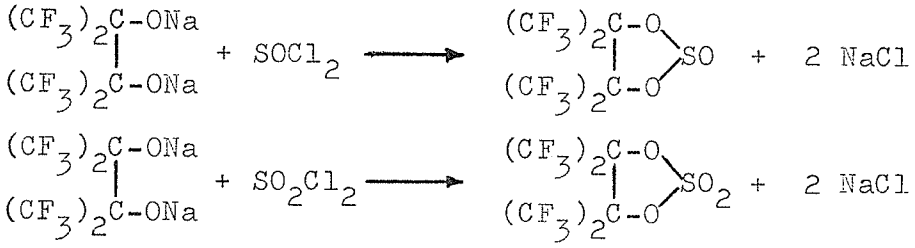
$$\begin{matrix}(CF_3)_2C\text{-}ONa\\ |\\ (CF_3)_2C\text{-}ONa\end{matrix} + (CH_3)_2MCl_2 \longrightarrow \begin{matrix}(CF_3)_2C\text{-}O\\ |\\ (CF_3)_2C\text{-}O\end{matrix}\!\!>\!M(CH_3)_2 + 2NaCl$$

M = Si, Ge or Sn

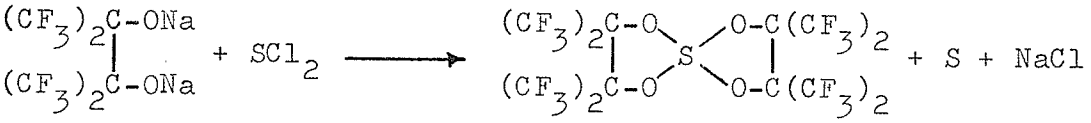
A boron-containing heterocycle was prepared by the reaction of phenylboron dichloride.



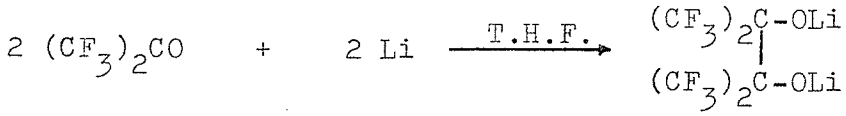
The reaction of the disodium alkoxide of perfluoropinacol with thionyl chloride or with sulphuryl chloride gave respectively the cyclic sulphite and sulphate.



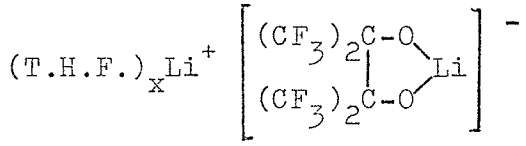
However, with sulphur dichloride, the reaction was more complicated and resulted in a volatile crystalline product which was a doubly cyclic derivative.



Other workers[35] prepared the dilithium perfluoropinacolate by passing hexafluoroacetone through pieces of lithium ribbon in tetrahydrofuran.



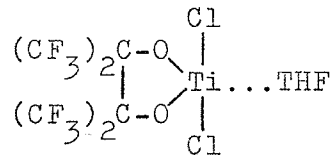
It was suggested that this compound may be a "pseudo-ring structure" described by,

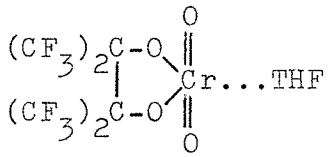


New members of the five-membered-ringed perfluoropinacol derivatives were prepared by the action of the dilithium salt on the appropriate reactants.

1. Y = C=O
2. Y = S=NCF$_3$
3. Y = S=NC$_2$F$_5$
4. Y = PC$_6$H$_5$

The titanium and chromium derivatives have a molecule of tetrahydrofuran associated with the metal.

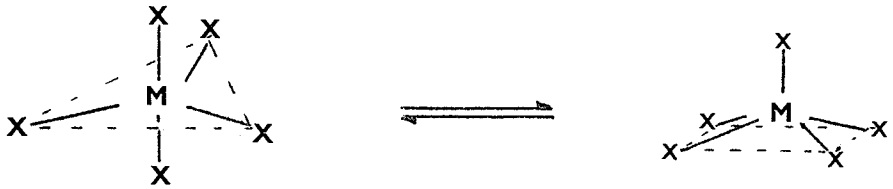




The stereochemistry of the trivalent and pentavalent oxidation states of Group V compounds has been investigated. Because of the existence of d orbitals for all the Group V elements except nitrogen, the stereochemistry of N(III) is considerably different from P(III) and As(III).

Sheldrick[36], by gas-phase electron-diffraction studies, showed that trisilylamine, $(SiH_3)_3N$, is coplanar, whereas the molecules of trisilylphosphine, $(SiH_3)_3P$, and trisilylarsine, $(SiH_3)_3As$, are pyramidal. The structure of trisilylamine was confirmed also by its infrared and Raman spectra. In these molecules, the stereochemistry certainly provides no direct evidence of p_{π}-d_{π} bonding.

The P(V) and As(V) stereochemistry is also very interesting to investigate. It was found[37] that there was only one peak in the fluorine n. m. r. spectrum of pentafluorophosphorus. Holmes and Deiters[38] found out that for the Group V compounds there exists an equilibrium between the trigonal bipyramidal and square pyramidal structures. Examples are PF_5, PCl_5, $SbCl_5$, $PClF_4$ and CH_3PF_4.

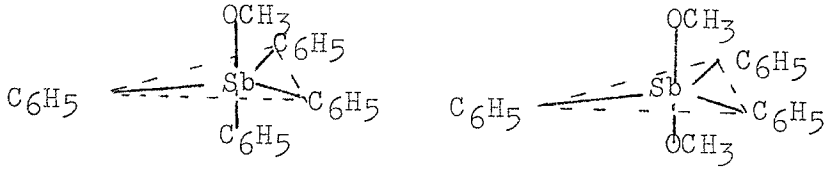


Such equilibrium is provided by the pseudorotation of the trigonal bipyramidal structure which requires only a low

activation energy.

The structure of antimony (V) has also been investigated. Pentaphenyl antimony[40] was found to have approximately square pyramidal molecular structure whereas the phosphorus and arsenic homologs adopt a trigonal bipyramidal geometry. The difference in energy between both structures for most compounds is probably small, and as such there may be specific ligand stabilization of either one of the states.

Shen[41] determined the structure of $(C_6H_5)_4Sb(OCH_3)$ and $(C_6H_5)_3Sb(OCH_3)_2$ by X-ray crystallography and confirmed their trigonal pyramidal structures.

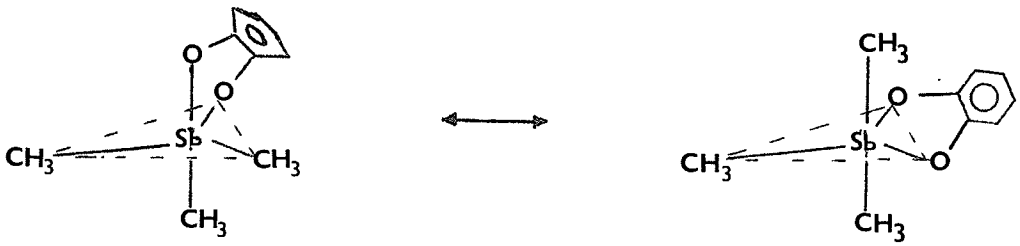


The latter structure was consistent with the result found by Shindo and Okawara[42] by studying the structures of other antimony(V) compounds such as

R_3SbX_2 X = Cl, Br, I, OCOR, $(C_2O_4)_{\frac{1}{2}}$, NO_3 or OCH_3

For these compounds, only the trigonal bipyramidal structure with the R-Sb group forming the trigonal plane and with the Cl or OCOR etc at the apices, had been found both in the solid and in solution.

The structure of trimethylantimony o-phenylenedioxides[42] was also determinedby proton n. m. r. The two isomers of trigonal bipyramids of this compound were in equilibrium in chloroform or methylene dichloride, probably through a square pyramidal intermediate.



The trifluoromethyl groups of the hexafluoroacetone can strongly reduce electron density on the adjacent carbonyl function. Thus reactions involving nucleophilic attack on the carbonyl carbon atom are favourable. Fluorinated alcohols are generally prepared by utilizing such properties.

$$(CF_3)_2CO + RH \longrightarrow RC(CF_3)_2OH$$

Hexafluoroacetone takes up water[43] to form the hexafluoroacetone hydrate which can be considered as an alcohol. Its decomposition by slight heating gives back the original reactants.

$$(CF_3)_2CO + H_2O \longrightarrow (CF_3)_2\underset{OH}{\overset{|}{C}}-OH$$

The photochemical irradiation of hexafluoroacetone and isopropyl alcohol yields perfluoropinacol[43].

$$(CF_3)_2CO + (CH_3)CHOH \xrightarrow{U.V.} \begin{matrix}(CF_3)_2C\text{-}OH \\ | \\ (CF_3)_2C\text{-}OH\end{matrix}$$

In the presence of tetrafluoroethylene, hexafluoroacetone and cesium fluoride yield the perfluoro-tertiary alcohol[44].

$$(CF_3)_2CO + CsF + C_2F_4 \xrightarrow{H^+} CF_3CF_2C(CF_3)_2OH$$

One of the stable fully fluorinated alcohols, the tris(pentafluorophenyl)carbinol[45], was synthesized by the reaction of decafluorobenzophenone with pentafluorophenyllithium (from C_6F_5Br + n-BuLi) in n-hexane solution at -78°.

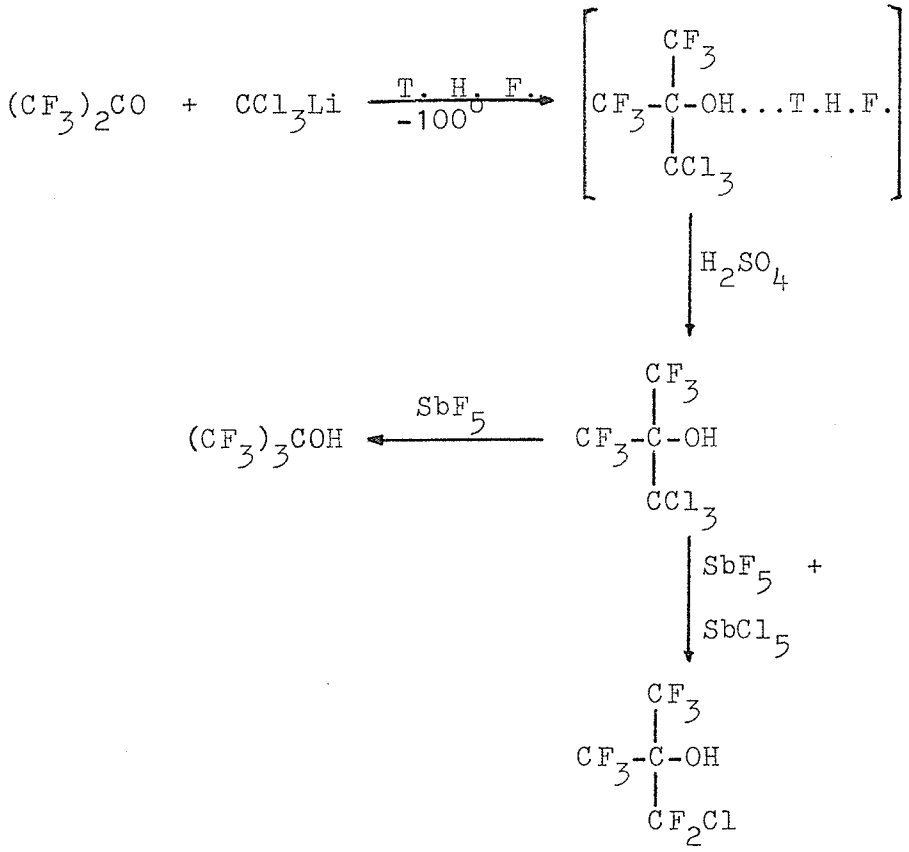
$$(C_6F_5)_2CO + C_6F_5Li \xrightarrow{n\text{-}C_6H_{14}} (C_6F_5)_3COH$$

It was found[46] that its solution in fluorosulphonic acid was stable and its fluorine n. m. r. spectrum showed the existence of tris(pentafluorophenyl)carbonium ion at -60°.

$$(C_6F_5)_3COH \xrightarrow{FSO_3H} (C_6F_5)_3C^+$$

Similarly, bis(pentafluorophenyl)methyl alcohol was prepared and its carbonium ion was studied.

However, the simplest example of the few fully fluorinated tertiary alcohols, perfluoro-t-butanol, was first reliably reported by Knunyants and Dyatkin[47] and by Filler and Schure[48]. The reaction scheme to produce this alcohol is shown as,



The object of this thesis was threefold, i.e. to study the nature of the perfluoroalkyl vicinal dihypochlorite, to study the reaction of disodium perfluoropinacolate with

some Group V compounds, and to attempt the preparation of some fluorinated alcohols via other simpler methods. Thus, this thesis can be conveniently divided into three parts:

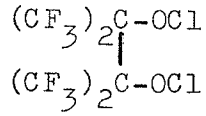
Part 1. Perfluoroalkyl Vicinal Dihypochlorite

Part 2. Disodium Perfluoropinacolate

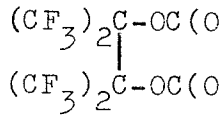
Part 3. Fluorinated Alcohols.

Some new compounds were prepared together with some known compounds during the course of this work. They are named as,

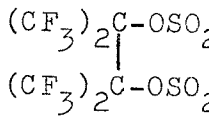
1. Perfluoroalkyl vicinal dihypochlorite, stands for



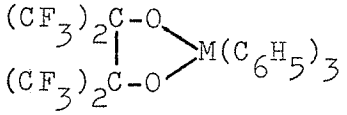
2. Perfluoroalkyl vicinal dichloroformate, stands for



3. Perfluoroalkyl vicinal dichlorosulphate, stands for

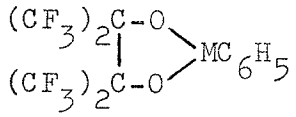


4. Triphenylphosphorus, triphenylarsenic or triphenylantimony perfluoropinacolate, stands for



where M = P, As or Sb respectively.

5. Phenylphosphorus or phenylarsenic perfluoropinacolate, stands for



where M = P or As respectively.

GENERAL PROCEDURE, REAGENTS AND APPARATUS

General

Conventional vacuum techniques were used throughout this work to effect preparation of reactants and separation of reaction products. Separation was obtained by use of various cold baths, e.g. acetone/dry ice (-78°), chloroform/liquid nitrogen (-63°), liquid nitrogen (-196°).

Reactions were carried out in sealed thick walled pyrex glass reaction ampoules. Experiments requiring ultra violet irradiation were performed in silica reaction tubes.

Chemicals

Hexafluoroacetone was a commercial sample (Matheson Chemical Company). Pentafluoromonochloroacetone was purchased from PCR Incorporated(Florida). Their purity was checked before use by infrared spectroscopy.

Chlorine gas, carbon monoxide and sulphur dioxide were used from commercial cylinders and dried before use by passing through concentrated sulphuric acid.

Sodium metal was cut free of the outer oxide layer under dry benzene. The oxide-free metal was further made into wire form from a sodium press before use.

The solvents were all carefully dried and distilled before use, e.g. tetrahydrofuran was dried by refluxing over lithium aluminium hydride for ten hours in a dry atmosphere (equipped with calcium sulphate tubes).

Instrumental

All infrared spectra were obtained on a Perkin Elmer 337 instrument using potassium bromide optics. The spectra were calibrated using a polystyrene film. Nuclear magnetic resonance spectra were obtained on a Varian Model A-56/60-A instrument, using 60 Mc/c and 56.4 Mc/s for proton and fluorine resonance respectively. The spectra were calibrated using internal standards. Tetramethylsilane and trichlorofluoromethane were used for the proton and fluorine standards respectively. Mass spectra were obtained on a Finnigan 1015 model with settings: manifold pressure around 10^{-7} torr, target current 500 μA and ionization voltage 70 $\pm$ 1 volts, unless otherwise mentioned. The resolution of the peak is approximately twice the mass number of the corresponding fragment of the molecule, as mentioned in the manual of the mass spectrometer. All ^{13}C peaks are not recorded in the tables of the mass spectra of various compounds for the sake of simplicity. Ultraviolet irradiation was provided by a Hanovia Utility U. V. Quartz Lamp at a distance of about 10 cm from the reaction vessel.

Elemental analyses were carried out by Dr. Alfred Bernhard at the Mikroanalitisches Laboratorium im Max-Planck-Institute, Mulheim, Germany.

EXPERIMENTAL

PART 1 Perfluoroalkyl Vicinal Dihypochlorite

Reaction of Perfluoropinacol with Chlorine in Trichlorofluoromethane

Perfluoropinacol was prepared from hexafluoroacetone and triethyl phosphite according to the method of Knunyants[24].

Dry chlorine gas slowly passed through a solution of perfluoropinacol (5.0 gm, 15.0 mmole) in trichlorfluoromethane (20 ml). The reaction vessel was contained in a cold bath at 0°C. After 20 minutes, dry nitrogen gas was introduced in order to remove excess chlorine.

The fluorine n. m. r. spectrum, taken immediately after the reaction, showed a singlet at 70.71 p.p.m. ($CFCl_3$ int. std.) due to unreacted perfluoropinacol. Infrared spectrophotometric examination showed the following absorption bands: 3660 (ms), 3500 (br, s), 1300 (s), 1275 (s), 1220 (s), 1120 (s), 1020 (s), 998 (s), 938 (s), 940 (s), 887 (s), 768 (ms), 750 (ms), 720 (ms), 680 (w), 558 (ms), 502 (w) and 490 (w). The product was identified as perfluoropinacol by comparision with an authentic sample.

Reaction of Disodium Perfluoropinacolate with Chlorine in Trichlorofluoromethane

Disodium perfluoropinacolate in tetrahydrofuran was prepared according to the method of Janzen and Willis[31]. Its reaction with chlorine was reported by Janzen and Pollitt[19].

Dry chlorine gas was slowly passed through a solution of disodium perfluoropinacolate (3.21 gm, 8.49 mmole/3 ml T. H. F.) in trichlorofluoromethane (30 ml) with stirring. The reaction vessel was contained in a cold bath at 0°. Reaction occurred and a white solid precipitated. After 20 minutes the reaction was stopped and the reaction solution quickly filtered.

The precipitate, presumably sodium chloride, gave a positive chloride test with silver nitrate solution.

The filtrate decomposed when attempts were made to remove the solvent or when it was kept above 0°.

The fluorine n. m. r. spectrum of the filtrate taken immediately after filtration showed a singlet at 70.57 p.p.m. ($CFCl_3$ int. std.). The infrared spectrum showed the lack of C=O or C=C absorption band and the presence of the perfluoroalkyl group absorption bands. These are consistent with the reported product, perfluoroalkyl vicinal dihypochlorite[19],

$$\begin{array}{l}(CF_3)_2C\text{-}OCl\\ \quad\quad|\\ (CF_3)_2C\text{-}OCl\end{array}$$

Reaction of Perfluoroalkyl Vicinal Dihypochlorite with Carbon Monoxide in Trichlorofluoromethane

A solution of perfluoroalkyl vicinal dihypochlorite (2.70 gm, 6.67 mmole/3 ml T.H.F.) in trichlorofluoromethane was prepared as described.

Dry carbon monoxide was slowly passed through a solution of perfluoroalkyl vicinal dihypochlorite in trichlorofluoromethane with stirring. The reaction vessel was contained in a cold bath at 0^{o}. After 20 minutes the reaction was stopped. Attempts to remove the solvent resulted in decomposition.

The fluorine n. m. r. spectrum of the solution taken directly after the preparation consisted of a singlet at 69.90 p.p.m. (int. std.). The infrared spectrum showed the lack of C=C absorption bands, but the presence of C=O band at 1795 cm^{-1} (s) showed the presence of chloroformate.[18] The presence of CF_3 absorptions at 1300 (s), 1275 (s) and 1220 (s) agreed with the expected absorption of the suggested product, perfluoroalkyl vicinal dichloroformate,

$$\begin{array}{l}(CF_3)_2C\text{-}OC(O)Cl\\ \quad\quad|\\ (CF_3)_2C\text{-}OC(O)Cl\end{array}$$

Reaction of Perfluoroalkyl Vicinal Dihypochlorite with Sulphur Dioxide in Trichlorofluoromethane

A solution of perfluoroalkyl vicinal dihypochlorite

(2.70 gm, 6.67 mmole/3 ml T.H.F.) in trichlorofluoromethane (30 ml) was prepared as described.

Dry sulphur dioxide was slowly passed through a solution of perfluoroalkyl vicinal dihypochlorite in trichlorofluoromethane with stirring. The reaction vessel was contained in a cold bath at 0°. After 20 minutes the reaction was stopped. Attempts to remove the solvent resulted in decomposition.

The fluorine n. m. r. spectrum of the solution taken directly after the preparation consisted of a singlet at 71.70 p.p.m. (int. std.). The infrared spectrum showed the lack of C=C absorption band, but the presence of S=O at 1440 (w) showed the presence of chlorosulphate.[18] The presence of CF_3 absorptions at 1300 (s), 1275 (s) and 1220 (s) agreed with the expected spectrum of the suggested product, perfluoroalkyl vicinal dichlorosulphate,

$$\begin{array}{l}(CF_3)_2C\text{-}OSO_2Cl\\ \quad\quad|\\ (CF_3)_2C\text{-}OSO_2Cl\end{array}$$

Reaction of Perfluoroalkyl Vicinal Dihypochlorite and Benzaldehyde in Carbon Tetrachloride

A solution of perfluoroalkyl vicinal dihypochlorite (8.10 gm, 20.0 mmole/9 ml T.H.F.) in trichlorofluoromethane (100 ml) was prepared as described. Most of the solvent was pumped off at -22°. Carbon tetrachloride (25 ml) was added. A solution of benzaldehyde (2.10 gm, 19.8 mmole) in carbon

tetrachloride (25 ml) was slowly added with stirring throughout. It was left to stand for 24 hours at -10°.

Most of the solvent was then pumped off. The fluorine n. m. r. spectrum of the residue taken showed singlets and triplets between 67.00 and 85.00 p.p.m. (int. std.) due to decomposed products. The infrared spectrum showed the presence of benzoic acid, small amount of benzoyl chloride and unreacted benzaldehyde when compared with spectra of authentic samples. Benzoic acid was recrystallized from hot water and was weighed (0.75 gm, 6.17 mmole).

The same procedure was repeated with reaction vessel irradiated with ultra violet light at 20° for 12 hours. Similar fluorine n. m. r. and infrared spectra were obtained.

Reaction of Perfluoropinacol with Benzoyl Chloride

Perfluoropinacol was prepared according to the method of Knunyants[24].

4.2 gm of benzoyl chloride (29.40 mmole) was added to 5.0 gm of perfluoropinacol (14.96 mmole). It was shaken for 20 minutes. Fluorine n.m.r. spectrum taken showed a singlet at 70.71 p.p.m. (int. std.) due to unreacted perfluoropinacol. The infrared spectrum showed that the substance was a mixture of the initial reactants when compared with the spectra of authentic samples.

The above procedure was repeated with the reaction vessel irradiated with ultra violet light for one hour at room temperature. Same results were observed.

Reaction of Perfluoroalkyl Vicinal Dihypochlorite with Triphenyl Phosphine in Carbon Tetrachloride

A solution of perfluoroalkyl vicinal dihypochlorite (8.10 gm, 20.0 mmole/9 ml T.H.F.) in trichlorofluoromethane (100 ml) was prepared as described. Most of the solvent was pumped off at -22°. Carbon tetrachloride (25 ml) was added. A solution of triphenyl phosphine (4.2 gm, 15.86 mmole) in 25 ml of carbon tetrachloride was also added. The solution was refluxed at 77° for 24 hours.

Most of the solvent was pumped off. The fluorine n. m. r. spectrum of the residue showed singlets and triplets between 67.00 and 85.00 p.p.m. (int. std.) due to the decomposed fluorinated products. Sublimation of the residue was carried out at 165° and at a pressure 10^{-3} mm. The sublimate (4.0 gm, 14.48 mmole) showed no fluorine n. m. r. absorption. Its infrared spectrum was identical to that of an authentic sample of triphenyl phosphorus oxide.

Same procedure was repeated with the reaction vessel irradiated with ultra violet light at room temperature for 24 hours. Most of the solvent was pumped off. The fluorine n. m. r. spectrum of the residue showed a similar pattern. Sublimation was carried out at 165° and at a pressure of 10^{-3} mm. The sublimate also showed no fluorine n. m. r. absorption. Its infrared spectrum was similar to that of triphenyl phosphorus oxide except that the absorption peaks were very much broader. It may be due to the formation of impurities besides the triphenyl phosphorus oxide, $(C_6H_5)_3PO$. However, no further investigation was undertaken.

PART 2 Disodium Perfluoropinacolate

Reaction of Hexafluoroacetone with Sodium

The reaction of hexafluoroacetone with sodium in tetrahydrofuran was reported by Janzen and Willis[31].

In a typical reaction, hexafluoroacetone (6.78 gm, 4.08 mmole) was transferred to a reaction tube partially filled with tetrahydrofuran (10 ml) and sodium metal (0.80 gm, 34.78 mmole). The sealed tube was shaken for 4 days at room temperature. The sodium reacted slowly to produce a solution that was free of sodium metal. The final solution was reddish brown in colour.

The solution was placed on a vacuum rack and the excess hexafluoroacetone was carefully removed. The solution was then carefully pumped upon to remove the majority of the solvent. The tetrahydrofuran that was removed was weighed to enable the amount of solvent remaining to be calculated. The disodium salt of perfluoropinacol that was prepared was stored under vacuum.

The fluorine n. m. r. spectrum in tetrahydrofuran gave a singlet at 71.8 p.p.m. (int. std). Infrared spectrum of a freshly prepared sample showed the following absorption bands (cm^{-1}): 1300 (ms), 1245 (s), 1182 (s), 1130 (s), 1110 (ms), 1050 (s), 985 (w), 955 (sm), 915 (w), 890 (w), 865 (ms), 732 (ms) and 712 (ms).

The procedure was repeated using benzene as solvent. After the sealed reaction tube was shaken for 5 days, it was observed that sodium metal remained undissolved. Hexafluoroacetone and benzene were recovered in the vacuum rack in unchanged quantities.

Reaction of Hexafluoroacetone with Triphenyl Phosphine in Tetrahydrofuran

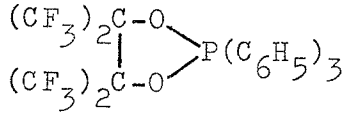
Triphenylphosphorus perfluoropinacolate was prepared from hexafluoroacetone and triphenyl phosphine similar to Stockel's method[26].

To a solution of triphenyl phosphine (4.50 gm, 17.18 mmole) in tetrahydrofuran (10 ml) in a reaction tube was added an excess of hexafluoroacetone (6.78 gm, 40.8 mmole). The tube was vacuum sealed and was shaken at room temperature for 2 days.

Vacuum fractionation of the reaction solution produced unreacted hexafluoroacetone and a white solid (10.20 gm, 17.18 mmole). The solid product (m. pt. 103°) was recrystallized from benzene.

The fluorine n. m. r. spectrum in tetrahydrofuran showed a singlet at 68.17 p.p.m. (int. std.). The infrared spectrum showed the expected C-H and C-F absorption bands and the characteristic five-membered-ring absorption bands[34].

The infrared spectrum (nujol) showed the following absorption bands (cm^{-1}): 3075 (w), 1580 (w), 1490 (w), 1431 (m), 1264 (bs), 1234 (bs), 1210 (bs), 1184 (s), 1108 (s), 1088 (s), 998 (m), 954 (ms), 878 (ms), 806 (ms), 764 (w), 744 (ms), 720 (s), 694 (s), 684 (w), 500 (s), 512 (w) and 488 (w). These were consistent with the structure of triphenylphosphorus perfluoropinacolate reported in literature[28].



A mass spectrum was taken. The result and analysis are shown in Table 4 and Figure 3 respectively.

Reaction of Hexafluoroacetone with Triphenyl Arsine in Tetrahydrofuran

To a solution of triphenyl arsine (5.0 gm, 16.3 mmole) in tetrahydrofuran (20 ml) was added excess hexafluoroacetone (6.7 gm, 40 mmole). The vacuum sealed reaction vessel was shaken for 5 days at room temperature.

Vacuum fractionation of the reaction solution yielded the starting materials in unchanged quantities.

The procedure was repeated with the reaction vessel irradiated with ultra violet light at 20° for 24 hours.

However, vacuum fractionation of the reaction solution again yielded the starting materials in unchanged quantities.

Reaction of Hexafluoroacetone with Triphenyl Antimony in Tetrahydrofuran

To a solution of triphenyl antimony (7.0 gm, 18.7 mmole) in tetrahydrofuran (20 ml) was added excess hexafluoroacetone (8.0 gm, 48.2 mmole). The vacuum sealed reaction tube was shaken for 5 days at room temperature.

Vacuum fractionation of the reaction solution yielded the starting materials in unchanged quantities.

The reaction was repeated by adding 0.1 gm of antimony metal (8.1 mmole) to the reaction solution as catalyst and shaken for 5 days at room temperature. Again vacuum fractionation of the reaction solution yielded the starting materials in unchanged quantities.

Reaction of Disodium Perfluoropinacolate with Triphenyl Phosphorus Dibromide in Tetrahydrofuran

To a solution of disodium perfluoropinacolate (2.30 gm, 8.32 mmole) in 25 ml of tetrahydrofuran was added a solution of triphenyl phosphorus dibromide (3.0 gm, 7.13 mmole) in 25 ml of tetrahydrofuran, drop by drop, at room temperature, with stirring throughout. Reaction occurred to precipitate a

white solid. After all the reactants were mixed, it was stirred for 2 hours.

The reaction solution was filtered. The precipitate (1.15 gm) presumably sodium bromide, gave a positive bromide test with silver nitrate solution. Vacuum fractionation of the reaction mixture produced the solvent and white solid. The solid product was recrystallized from ethanol.

The fluorine n. m. r. spectrum, in tetrahydrofuran, showed a singlet at 68.17 p.p.m. (int. std.). The infrared spectrum was identical to the spectrum of the product from the reaction of hexafluoroacetone and triphenyl phosphine. Thus triphenylphosphorus perfluoropinacolate was also obtained.

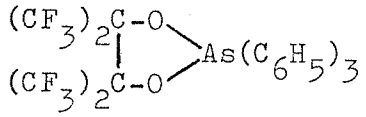
Reaction of Disodium Perfluoropinacolate with Triphenyl Arsenic Dichloride in Tetrahydrofuran

Hexafluoroacetone (6.7 gm, 40.2 mmole) was transferred to a reaction tube partially filled with tetrahydrofuran (10 ml), sodium metal (0.80 gm, 34.78 mmole) and triphenyl arsenic dichloride (6.0 gm, 15.9 mmole). The sealed tube was shaken for 5 days at room temperature. The sodium reacted slowly to produce a yellow solution and a white solid precipitated out.

The reaction solution was filtered. The precipitate (1.00 gm), presumably sodium chloride, gave a positive chloride

test with silver nitrate solution. Vacuum fractionation of the reaction mixture yielded the solvent and a white solid. The solid product was recrystallized from ethanol (m. p. 120°). It was found to decompose on sublimation or at room temperature in a few days, hexafluoroacetone being liberated.

The fluorine n. m. r. spectrum in trichlorofluoromethane showed a singlet at 67.85 p.p.m. (int. std.). The infrared spectrum showed the expected C-H and C-F absorption bands and the characteristic five-membered-ring absorption bands. The infrared spectrum (nujol) is recorded (cm^{-1}): 3076 (bm), 1580 (w), 1490 (m), 1431 (s), 1264 (bs), 1234 (bs), 1210 (bs), 1147 (s), 1107 (s), 1072 (s), 1023 (m), 996 (ms), 990 (m), 950 (s), 874 (s), 762 (ms), 737 (s), 717 (s), 689 (s), 661 (w), 537 (w) and 473 (s). These were consistent with the suggested structure of triphenylarsenic perfluoropinacolate.



A mass spectrum of the product was taken. Its result is shown in Table 5.

Anal. Calcd. for $C_{24}H_{15}F_{12}O_2As$: C, 45.10; H, 2.35; F, 35.75. Found: C, 48.10; H, 2.76; F, 35.29. This corresponds to 94 % of the product and 6 % of triphenyl arsine.

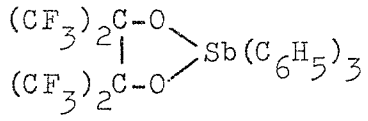
Reaction of Disodium Perfluoropinacolate with Triphenyl Antimony Dichloride in Tetrahydrofuran

To a solution of disodium perfluoropinacolate (2.30 gm, 8.32 mmole) in 25 ml. of tetrahydrofuran was added a solution of triphenyl antimony dichloride (3.00gm, 7.07 mmole) in 25 ml of tetrahydrofuran, drop by drop, at room temperature, with stirring throughout. Reaction occurred and a white solid precipitated. After all the reactants were mixed, it was stirred for 2 hours.

The reaction solution was filtered. The precipitate (0.5 gm), presumably sodium chloride, gave a positive chloride test with silver nitrate solution. Vacuum fractionation of the reaction mixture yielded the solvent and a white solid. The solid product was recrystallized from ethanol (m. p. 110°). It decomposed on sublimation or on standing at room temperature in few days.

The fluorine n. m. r. spectrum in trichlorofluoromethane showed a singlet at 68.89 p.p.m. (int. std.). The infrared spectrum showed the expected C-H and C-F absorption bands and the absorption bands characteristic of the five-membered cyclic system. The infrared spectrum (nujol) showed the following absorption bands: 3076 (bm), 1580 (w), 1490 (m), 1431 (s), 1266 (bs), 1236 (bs), 1196 (s), 1152 (s), 1111 (s), 1064 (m), 996 (m), 990 (mw), 950 (s), 871 (sm), 756 (m), 731 (s), 711 (s), 685 (s), 656 (w), 518 (w) and 447 (m).

These were consistent with the suggested structure of triphenylantimony perfluoropinacolate.



A mass spectrum of the product was taken. Its result and analysis are shown in Table 6 and Figure 4 respectively.

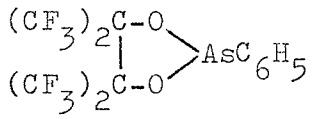
Anal. Calcd. for $C_{24}H_{15}F_{12}O_2Sb$: C, 42.15; H, 2.19; F, 33.35. Found: C, 33.52; H, 1.79; F, 28.75. This corresponds to 80 % of the product and 20 % of antimony oxide, Sb_2O_3.

Reaction of Disodium Perfluoropinacolate with Phenyl Arsenic Dichloride in Acetonitrile

To a solution of disodium perfluoropinacolate (4.60 gm, 16.64 mmole) in 50 ml of acetonitrile was added a solution of phenyl arsenic dichloride (3.10 gm, 14.55 mmole) in 25 ml of acetonitrile, drop by drop, at room temperature, with stirring throughout. Reaction occurred and a white solid precipitated. After all the reactants were mixed, it was stirred for 2 hours.

The reaction solution was filtered. The precipitate (1.00 gm), presumably sodium chloride, gave a positive chloride test with silver nitrate solution. Vacuum distillation (10^{-3} mm) at 125^{o} yielded pale yellow liquid.

The fluorine n. m. r. spectrum in trichlorofluoromethane appeared as two broad multiplets (Figure 3) of equal areas centered at 67.15 and 67.90 p.p.m. (int. std.). The infrared spectrum showed the expected C-H and C-F absorption bands and the characteristic five-membered-ring absorption bands. It is recorded as follows (cm^{-1}): 1448 (w), 1264 (bs), 1239 (bs), 1207 (bs), 1089 (sm), 1074 (m), 990 (w), 939 (m), 869 (mw), 760 (w), 730 (ms), 710 (m) and 685 (m). These were consistent with the suggested structure of phenylarsenic perfluoropinacolate.



A mass spectrum was taken. Its result and analysis are shown in Table 8 and Figure 6 respectively.

Anal. Calcd. for $C_{12}H_5F_{12}O_2As$: C, 29.75; H, 1.03; F, 47.08. Found: C, 31.37; H, 1.42; F, 37.54. This corresponds to 80 % of the product and 20 % of phenyl arsenic dichloride.

Reaction of Disodium Perfluoropinacolate with Tetraphenyl Arsenic Chloride

To a solution of tetraphenyl arsenic chloride (5.40 gm, 13.9 mmole) in 25 ml of ethanol was added a solution of disodium perfluoropinacolate (4.60 gm, 16.64 mmole) in 50 ml of tetrahydrofuran, drop by drop, at room temperature, with stirring throughout. Reaction occurred and white solids precipitated. After all the reactants were mixed, it was stirred for 2 hours.

The reaction solution was filtered. The fluorine n. m. r. spectrum of the filtrate showed no fluorine absorption. Thus the precipitate was stirred in 50 ml of acetonitrile for another 2 hours. It was filtered. The residue, presumably sodium chloride, gave a positive chloride test with silver nitrate solution. The fluorine n. m. r. spectrum of the filtrate showed a singlet at 71.26 p.p.m. (int. std.).

The product decomposed when attempt was made to remove all the solvent. However, after most of the solvent was removed, its infrared spectrum showed absorption bands at the CF_3 region, but the characteristic bands of the five-membered cyclic system were absent.

Recrystallization of the product in ether resulted in a compound identified as triphenyl arsenic oxide when its infrared spectrum was compared with that of the sample prepared from the oxidation of hydrogen peroxide on triphenyl arsine[49].

PART 3 Fluorinated Alcohols

Preparation of Perfluoropinacol

The preparation of perfluoropinacol was similar to Knunyants's method[24].

Hexafluoroacetone (10.0 gm, 60.15 mmole) was added to a neat sample of triethyl phosphite $(C_2H_5O)_3P$ (5.6 gm, 33.8 mmole) in a reaction tube. The vacuum sealed tube was shaken for five days at room temperature. The reaction product was identified by infrared spectroscopy as a 2:1 adduct of hexafluoroacetone and triethyl phosphite[23].

The product was shaken with 20 ml of concentrated sulphuric acid to yield colorless crystals. The crystals were dissolved in 100 ml of water and boiled for one hour. The mixture was cooled and 20 ml of sulphuric acid was carefully added. Two layers gradually appeared. It was left to stand for 12 hours.

The bottom layer, separated out by separatory funnel, was mixed with an equal amount of concentrated sulphuric acid and was distilled. Distillate was collected at 112^{o}.

The product was identified as perfluoropinacol by fluorine n. m. r. and infrared spectroscopy[24]. The fluorine n. m. r. spectrum showed a singlet at 70.71 p.p.m. (int. std.). Infrared spectrum showed the following absorption bands (cm^{-1}):

3660 (ms), 3500 (bs), 1275 (s), 1220 (s), 1120 (s), 1020 (s), 998 (s), 958 (s), 940 (s), 882 (s), 768 (ms), 750 (ms), 720 (ms), 680 (w), 650 (w), 558 (ms), 502 (w) and 490 (w).

The mass spectrum of the product was taken. Its result and analysis are shown in Table 9 and Figure 7 respectively.

Reaction of Hexafluoroacetone with Chloroform

To 4.82 gm of chloroform in a reaction tube (40.40 mmole) was added 6.7 gm of hexafluoroacetone (40.40 mmole). The tube was carefully vacuum sealed and was shaken for 3 days at room temperature.

It was discovered that hexafluoroacetone was not miscible with chloroform. The proton n. m. r. spectrum of the chloroform layer showed a singlet at 2.87 τ due to chloroform (T.M.S. int. std.). The fluorine n. m. r. spectrum, however, showed a singlet at 74.50 p.p.m. (int. std.) due to hexafluoroacetone which is slightly soluble in chloroform. Vacuum fractionation of the chloroform layer produced unreacted chloroform (original quantity) and a little hexafluoroacetone.

The experiment was repeated. The sealed tube containing chloroform (4.82 gm) and hexafluoroacetone (6.7 gm) was irradiated with ultra violet light for 24 hours. Infrared spectrum of the reaction solution showed absorption at 3570 cm^{-1} and other peaks besides the chloroform bands. Proton n. m. r.

showed a singlet at 2.87 τ due to chloroform and a small broad singlet at 6.04 τ . The fluorine n. m. r. showed a singlet at 67.45 p.p.m. (int. std.). The new peaks of the spectra were consistent with the alcohol $(CF_3)_2C(CCl_3)OH$ reported by Filler and Schure[48].

Reaction of Hexafluoroacetone with Chloroform in Tetrahydrofuran

To a solution of chloroform (8.50 gm, 71.60 mmole) in 15 ml of tetrahydrofuran was added 13.10 gm of hexafluoroacetone (78.95 mmole) in a reaction tube. The tube was carefully vacuum sealed and was irradiated with ultra violet light at 35° for 24 hours.

Vacuum fractionation of the reaction solution produced tetrahydrofuran, unreacted hexafluoroacetone and chloroform and left a yellow involatile liquid. The liquid was shaken with 10 % hydrochloric acid. The heavier immiscible fraction was added with 15 ml of concentrated sulphuric acid and was vacuum distilled (10^{-3} mm) at 76° for 16 hours. A colorless liquid was collected in the carbon dioxide/acetone bath (-78°). The weight was 2.0 gm. Infrared spectroscopic examination showed that the major component was perfluoropinacol by comparison with the spectrum of an authentic sample.

Fluorine n. m. r. spectrum showed a singlet at 70.71 p.p.m. due to perfluoropinacol and a doublet at 76.60 p.p.m. (J = 6 cps.) (int. std.), the integrated area ratio being 5:1. Proton n. m. r. spectrum showed a singlet at 5.31 τ due to perfluoropinacol and a weak septet centered at 5.63 τ (J = 6 cps.). These observations were consistent with the presence of $(CF_3)_2CHOH$ reported by Middleton and Lindsey[43].

Reaction of Pentafluorochloroacetone with Chloroform

To 2.63 gm of chloroform in a reaction tube (22.0 mmole) was added 4.0 gm of pentafluorochloroacetone (21.9 mmole). The tube was carefully vacuum sealed and was shaken for 3 days at room temperature.

It was discovered that the pentafluorochloroacetone was not miscible with chloroform. The proton n. m. r. spectrum of the chloroform layer showed a singlet at 2.87 τ due to chloroform. The fluorine n. m. r. spectrum, however, showed a triplet at 72.95 p.p.m. (J = 8 cps.) and a quartet at 66.40 p.p.m. (J = 8 cps.) with integrated area ratio 3:2 due to the pentafluorochloroacetone which dissoves slightly in chloroform. Vacuum fractionation of the chloroform layer produced unreacted chloroform (original quantity) and a little pentafluorochloroacetone.

The experiment was repeated. The sealed tube containing

chloroform (2.63 gm) and pentafluorochloroacetone (4.0 gm) was irradiated with ultra violet light for 24 hours. Infrared spectrum of the reaction solution showed absorption at 3570 cm^{-1} and others besides the chloroform bands. Proton n. m. r. spectrum showed a singlet at 2.87 τ due to chloroform and a small broad singlet at 6.18 τ . The fluorine n. m. r. spectrum showed a triplet at 73.20 p.p.m. (J = 8 cps.) and a quartet at 66.00 p.p.m. (J = 8 cps.) (int. std.), the ratio of the integrated areas being 3:2. Comparing the data with those of $(CF_3)_2C(CCl_3)OH$ reported by Filler and Schure[48], it might be suggested that $CF_3C(CF_2Cl)(CCl_3)OH$ was present.

Reaction of Pentafluorochloroacetone with Chloroform in Tetrahydrofuran

To a solution of 2.63 gm of chloroform (22.0 mmole) in 10 ml of tetrahydrofuran was added 4.0 gm of pentafluorochloroacetone (21.9 mmole) in a reaction tube. The tube was carefully vacuum sealed and was irradiated with ultra violet light at room temperature for 24 hours.

Vacuum fractionation of the reaction solution produced tetrahydrofuran, unreacted pentafluorochloroacetone and chloroform and left a yellow involatile liquid. The fluorine n. m. r. showed three sets of doublets of triplets centered at 71.80, 72.55 and 74.37 p.p.m. (CF_3 region) and

two sets of multiplets centered at 59.70 and 60.73 p.p.m. (CF_2Cl region) (int. std.). The proton n. m. r. spectrum showed, besides the chloroform and tetrahydrofuran peaks, a quartet of doublets of doublets centered at 5.42 τ . The patterns of the fluorine and proton splittings are similar to the $CH(CF_3)(CF_2Cl)$- group of the silicon compounds synthesized by Begleiter, Chan and Janzen[50]. Since the infrared spectrum showed no sign of any O-H absorption, the work was not continued.

DISCUSSION

PART 1 Perfluoroalkyl Vicinal Dihypochlorite

The synthesis and study of alkyl hypochlorites have been investigated for more than a hundred years. However, little success has been achieved due to the difficulties to isolate the compounds. Tertiary butyl hypochlorite[8,3] is the most stable compound of this class known so far.

The first perfluorohypochlorites, CF_3OCl and iso-C_3F_7OCl were synthesized by Fox[51] in 1968 by the action of ClF on $F_2C{=}O$ and $(CF_3)_2C{=}O$ respectively with CsF as catalyst.

$$F_2C{=}O + ClF \longrightarrow CF_3OCl$$

$$(CF_3)_2C{=}O + ClF \longrightarrow \text{iso-}C_3F_7OCl$$

Recently, Fox successfully prepared the same class of compound by the reaction of ClF on perfluoro-alcohols[18].

$$ROH + ClF \longrightarrow ROCl + HF$$

During the course of his work, he tried to prepare the perfluoroalkyl vicinal dihypochlorite by reacting ClF with perfluoropinacol. However, only decomposition products resulted.

On studying the characteristics of these perfluoroalkyl hypochlorites, he and his coworkers discovered that carbon monoxide and sulphur dioxide can insert into the O-Cl bond to form the chloroformate and chlorosulphate respectively.

$$ROCl + CO \longrightarrow ROC(O)Cl$$

$$ROCl + SO_2 \longrightarrow ROSO_2Cl$$

where R = $(CF_3)_3C$, $(CF_3)_2CH$, $CH_3C(CF_3)_2$ or CF_3CH_2.

However, recently, Janzen and Pollitt[19] successfully prepared the very unstalbe perfluoroalkyl vicinal dihypochlorite by the action of chlorine on disodium perfluoropinacolate in trichlorofluoromethane solution at low temperature.

$$\begin{matrix}(CF_3)_2C\text{-}ONa \\ | \\ (CF_3)_2C\text{-}ONa\end{matrix} + Cl_2 \longrightarrow \begin{matrix}(CF_3)_2C\text{-}OCl \\ | \\ (CF_3)_2C\text{-}OCl\end{matrix} + NaCl$$

This compound is characterized by the fluorine n. m. r. and infrared data and also by the reactions:
1. its preparation in protic solvent results in perfluoropinacol,
2. reaction with benzaldehyde produces benzoyl chloride and benzoic acid.

One of the objects of this thesis is to further characterize this dihypochlorite by the insertion reactions analogous to Fox's and other reactions by ultilizing the oxidising property of this dihypochlorite.

The attempt to produce perfluoroalkyl vicinal dihypochlorite by passing chlorine through perfluoropinacol ends up with no reaction. This behaviour is very different from the nonfluorinated alkyl alcohol such as ethyl alcohol[3].

$$C_2H_5OH + Cl_2 \longrightarrow C_2H_5OCl$$

$$\begin{matrix}(CF_3)_2C\text{-}OH \\ | \\ (CF_3)_2C\text{-}OH\end{matrix} + Cl_2 \longrightarrow \text{no reaction}$$

The existence of perfluoroalkyl vicinal dihypochlorite can further be justified by the carbon monoxide and sulphur dioxide insertion reactions.

$$\begin{matrix}(CF_3)_2C\text{-}OCl \\ | \\ (CF_3)_2C\text{-}OCl\end{matrix} + 2CO \longrightarrow \begin{matrix}(CF_3)_2C\text{-}OC(O)Cl \\ | \\ (CF_3)_2C\text{-}OC(O)Cl\end{matrix}$$

$$\begin{matrix}(CF_3)_2C\text{-}OCl \\ | \\ (CF_3)_2C\text{-}OCl\end{matrix} + 2SO_2 \longrightarrow \begin{matrix}(CF_3)_2C\text{-}OSO_2Cl \\ | \\ (CF_3)_2C\text{-}OSO_2Cl\end{matrix}$$

The resulting products are named as perfluoroalkyl vicinal dichloroformate and dichlorosulphate respectively.

Existence and Stability

Similar to the perfluoroalkyl vicinal dihypochlorite[19], the dichloroformate and dichlorosulphate of the same family decompose readily when they are kept at room temperature or

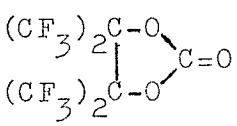
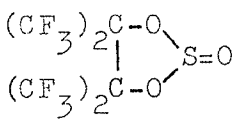
when solvent is taken away, and therefore no elemental analyses were possible to obtain. Their existence can only be supported by their spectrophotometric behaviour. Like the perfluoroalkyl vicinal dihypochlorite, the infrared spectra of the dichloroformate and dichlorosulphate show broad and strong absorption bands in the regions 1210 - 1260 cm^{-1} as well as sharp and medium absorptions between 690 and 725 cm^{-1} which can be assigned to CF_3 stretching modes. Also, no C=C or O-H absorptions are observed. However, unlike the dihypochlorite, a strong C=O peak (1795 cm^{-1}) and a weak S=O peak (1440 cm^{-1}) are found in the spectra of dichloroformate and dichlorosulphate respectively. These absorptions are consistent with the C=O and S=O peaks of Fox's chloroformates and chlorosulphates[18]. No characteristic absorptions due to the five-membered chelate ring are present eliminating the possible formations of  and  . Their fluorine n. m. r. spectra show singlets at 69.90 p.p.m. and 71.70 p.p.m. respectively (the dihypochlorite shows a singlet at 70.57 p.p.m.), both being in the CF_3 region (Table 1). In each case, the singlet means that all six fluorine atoms are magnetically equivalent, consistent with the suggested formulae of the compounds. However, to further support the existence of the dichloroformate and dichlorosulphate, more characterisation by means of their reactions with some other

Table 1

Spectroscopic Properties of Perfluoroalkyl Vicinal Compounds*.

Compounds	^{19}F n.m.r.	I.R.(C=O;S=O)
Dihypochlorite $(CF_3)_2C(OCl)C(CF_3)_2OCl$	70.57 p.p.m. (singlet)	No absorption
Dichloroformate $(CF_3)_2C(OC(O)Cl)C(CF_3)_2OC(O)Cl$	69.90 p.p.m. (singlet)	1795 cm^{-1}(s) (C=O)
Dichlorosulphate $(CF_3)_2C(OSO_2Cl)C(CF_3)_2OSO_2Cl$	71.70 p.p.m. (singlet)	1440 cm^{-1}(w) (S=O)

*Solvent: trichlorofluoromethane

compounds still has to be done, since elemental analyses are not possible.

Besides the intense CF_3 singlet, the fluorine n. m. r. spectrum of the perfluoroalkyl vicinal dihypochlorite also shows few doublets and triplets between 68 and 78 p.p.m., which are much less intense. These are believed to arise from the decomposition of some dihypochlorite during the passing of chlorine through the disodium perfluoropinacolate solution. The same pattern of fluorine n. m. r. spectrum is observed after carbon monoxide or sulphur dioxide is passed through the trichlorofluoromethane solution of the dihypochlorite, showing no sign of further decomposition. The dichloroformate so formed decomposes slowly at room temperature whereas the dichlorosulphate seems to be stable at the same condition. All these compounds decompose readily when heat is applied or attempt is made to remove the solvent. On these bases, it is reasonable to conclude that the stability of these compounds follows the order,

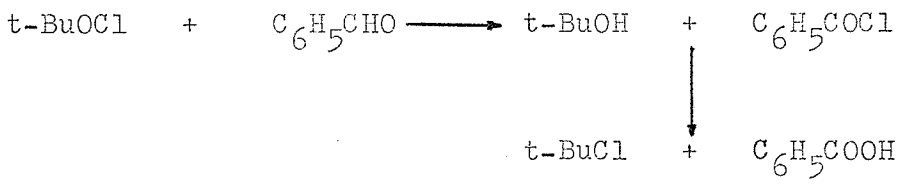
$$\begin{array}{c}(CF_3)_2COSO_2Cl\\ |\\ (CF_3)_2COSO_2Cl\end{array} > \begin{array}{c}(CF_3)_2COC(O)Cl\\ |\\ (CF_3)_2COC(O)Cl\end{array} > \begin{array}{c}(CF_3)_2COCl\\ |\\ (CF_3)_2COCl\end{array}$$

Oxidation Mechanism of Perfluoroalkyl Vicinal Dihypochlorite

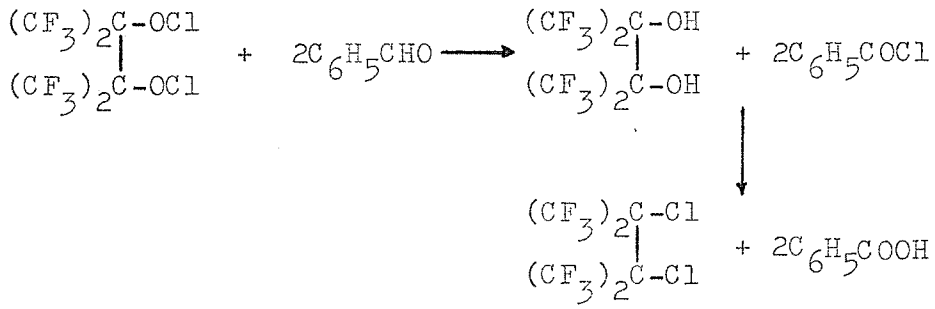
The existence of perfluoroalkyl vicinal dihypochlorite is also supported by chemical reactions studied by Janzen and

Pollitt[19]. They discovered that when preparation of dihypochlorite was carried out in tetrahydrofuran, the final product was perfluoropinacol, indicating hydrogen abstraction from solvent. It is well known that the analogous reaction of tertiary butyl hypochlorite and hydrocarbon solvents gives t-butyl alcohol[52].

If benzaldehyde is added to a solution of dihypochlorite in carbon tetrachloride, the main products are benzoic acid and benzoyl chloride. These products are also found when t-butyl hypochlorite reacts with benzaldehyde in carbon tetrachloride[9].



If a reaction scheme was ratioanalized analogous to the hydrocarbon reaction,



it would suffer two defects. Firstly, the chloride $(CF_3)_2C(Cl)C(CF_3)_2Cl$ has never been isolated or identified. Instead, the fluorinated end products from the reaction were decomposed materials. Secondly, when perfluoropinacol was added to benzoyl chloride, with slight heating or with ultra violet irradiation, no reaction was apparent. Thus, they cannot be considered as the intermediates of the described reaction.

Perfluoroalkyl vicinal dihypochlorite oxidizes triphenyl phosphine to triphenyl phosphoric oxide with heating or ultra violet irradiation.

$$\begin{matrix}(CF_3)_2C\text{-}OCl \\ | \\ (CF_3)_2C\text{-}OCl\end{matrix} \quad + \quad (C_6H_5)_3P \longrightarrow (C_6H_5)_3P{=}O$$

Based on such behaviours of the perfluoroalkyl vicinal dihypochlorite, no satisfactory mechanism can be employed to explain the observed phenomena. It is possible that in the presence of ultra violet light or heat, the unstable perfluoroalkyl vicinal dihypochlorite decomposes and generates the chlorine or oxygen radicals (Cl· or O·) which are responsible for oxidizing the benzaldehyde and triphenyl phosphine.

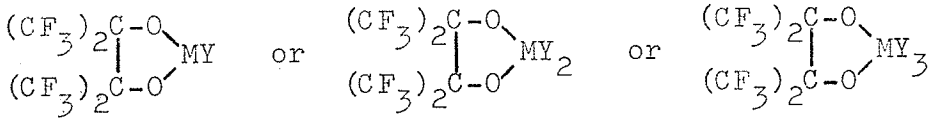
PART 2 Disodium Perfluoropinacolate

It is well known that the action of an alkali metal on hexafluoroacetone, $(CF_3)_2CO$, in a suitable donor solvent, is to produce a di-metallic perfluoropinacolate.

$$(CF_3)_2C{=}O + Na \longrightarrow \begin{matrix}(CF_3)_2C\text{-}ONa\\ |\\ (CF_3)_2C\text{-}ONa\end{matrix}$$

$$(CF_3)_2C{=}O + Li \longrightarrow \begin{matrix}(CF_3)_2C\text{-}OLi\\ |\\ (CF_3)_2C\text{-}OLi\end{matrix}$$

The high reactivity of the ionic alkoxide makes it a valuable intermediate for the preparation of perfluoropinacol derivatives by the reaction with halides of other elements. The structure of the ion suggests that five-membered chelate rings should be readily formed by reaction with dihalides. By reaction of the dihalo compounds with the sodium or lithium perfluoropinacolate, the corresponding derivatives have been prepared[23-29], which are summarized in the General Introduction.

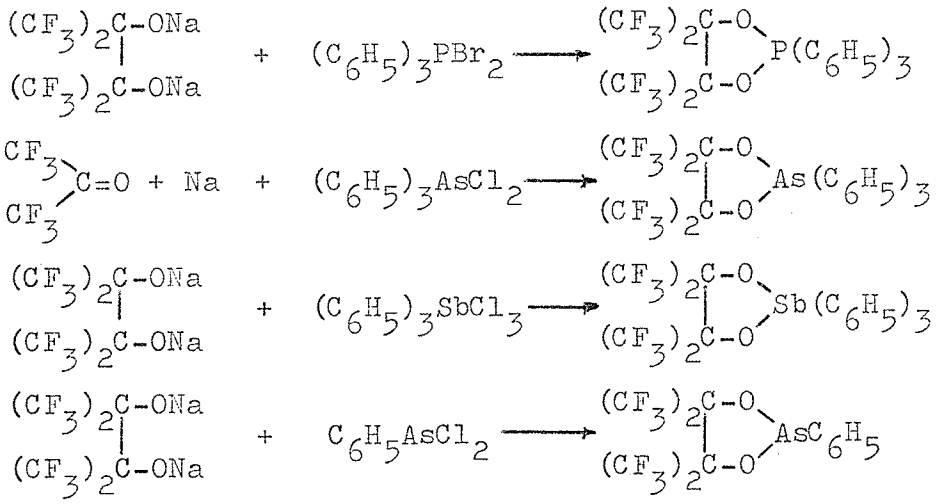


All these compounds are characterised with the characteristic infrared absorption frequencies in five

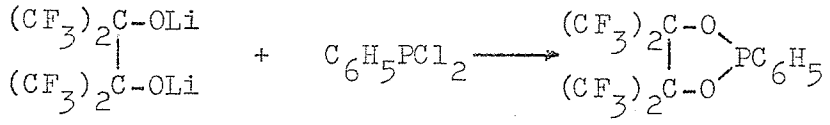
regions[34], 1080 - 1120 cm^{-1} (s or m), 992 - 1007 cm^{-1} (m or w), 920 - 969 cm^{-1} (s or m), 882 - 889 cm^{-1} (s or m) and 735 - 750 cm^{-1} (s or m).

Characteristic Infrared Absorption

Four compounds are prepared contributing to part of the work of this thesis. They are the triphenylphosphorus, triphenylarsenic, triphenylantimony and phenylarsenic perfluoropinacolates prepared from the disodium perfluoropinacolate solution.



Conroy and Dresdner[35] prepared the phenylphosphorus perfluoropinacolate from the dilithium perfluoropinacolate solution and reported its infrared spectrum.



It is found that the characteristic frequencies of the five-membered chelate ring are also present in the infrared spectra of the above perfluoropinacol derivatives. These are listed in Table 2 and the spectra are shown in Figure 1.

Stability

The stability of triphenylphosphorus, triphenylarsenic and triphenylantimony perfluoropinacolates has been investigated. The triphenylphosphorus perfluoropinacolate shows no sign of decomposition after keeping in a stoppered bottle for a month, whereas the corresponding arsenic and antimony compounds decompose in a few days. The phosphorus compound can be easily recrystallized from benzene or ethanol for purification, but benzene is found unsuitable for purifying the arsenic or antimony analogues. Ethanol has to be used. When an attempt is made to purify the crystals of the arsenic derivative through vacuum sublimation at 120°, hexafluoroacetone is given off identified from its infrared spectrum. The vacuum sublimation of the antimony compound results in more than one volatile gas, one of them being hexafluoroacetone. Thus it can be concluded that triphenyl-phosphorus perfluoropinacolate is much more stable than the triphenylarsenic or triphenylantimony perfluoropinacolates.

Hexafluoroacetone reacts with triphenyl phosphine to form the triphenylphosphorus perfluoropinacolate. No reaction

Table 2

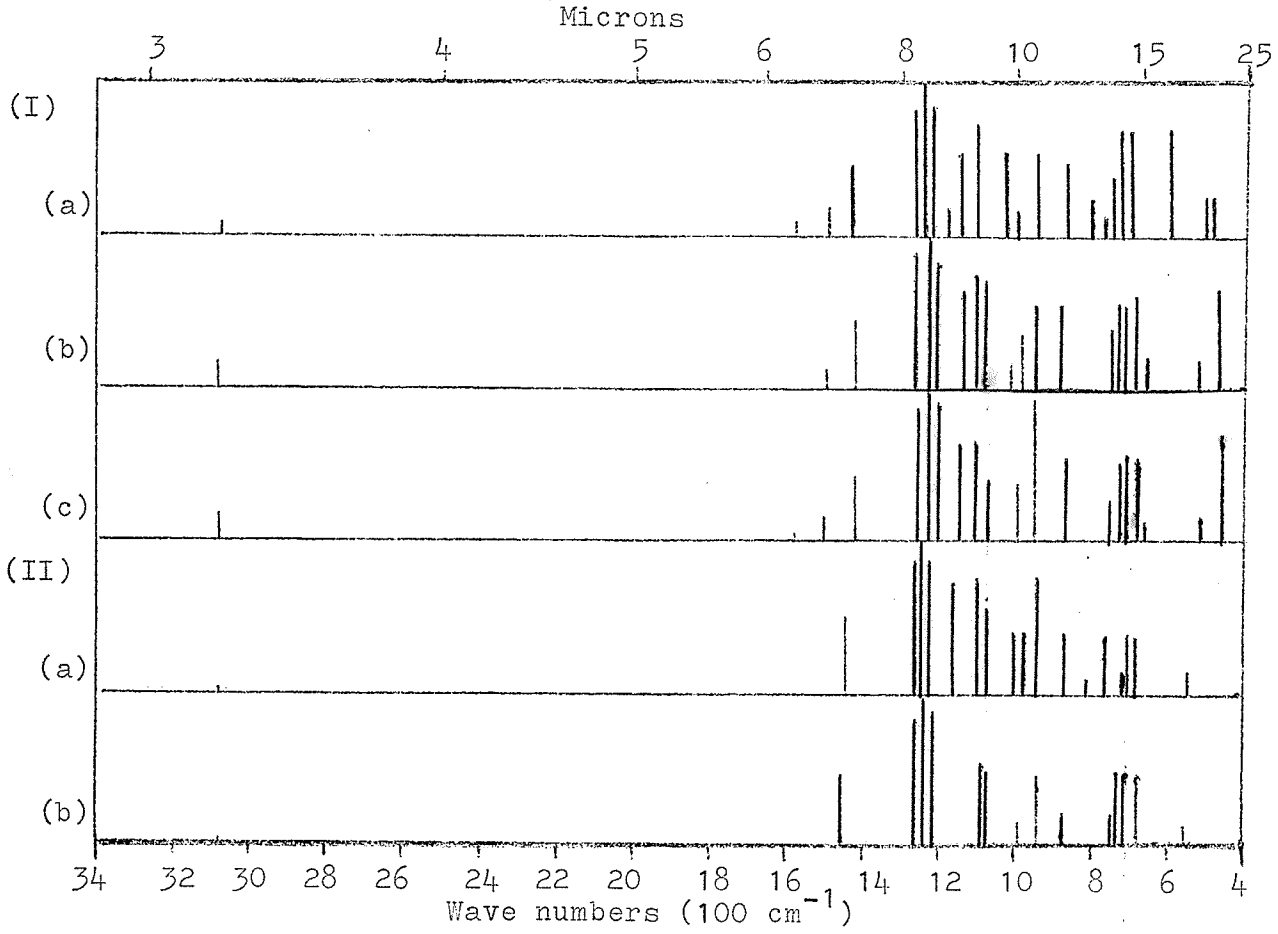
Characteristic Infrared Absorption (cm^{-1}) of Group V Perfluoropinacol Derivatives

Compounds	Mode	I. R. Spectral Data				
$(C_6H_5)_3P(PFP)^*$	Nujol	1108(m)	998(w)	954(m)	878(m)	744(m)
$(C_6H_5)_3As(PFP)$	Nujol	1107(s)	996(m)	950(m)	874(m)	737(s)
$(C_6H_5)_3Sb(PFP)$	Nujol	1111(m)	996(w)	950(s)	871(m)	731(s)
$C_6H_5P(PFP)$	Neat	1100(s)	975(w)	950(m)	885(m)	755(m)
$C_6H_5As(PFP)$	Neat	1089(m)	990(w)	939(m)	869(m)	730(s)

*PFP stands for perfluoropinacolate, $-OC(CF_3)_2C(CF_3)_2O-$.

Figure 1

Infrared Spectra of Group V Derivatives of Perfluoropinacol



Infrared spectra of:

(I) $(CF_3)_2C(O)$ / $(CF_3)_2C(O)$ $M(C_6H_5)_3$

(a) M = P

(b) M = As

(c) M = Sb

(II) $(CF_3)_2C(O)$ / $(CF_3)_2C(O)$ MC_6H_5

(a) M = P

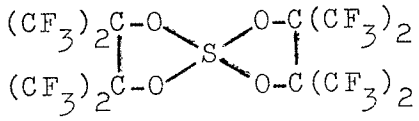
(b) M = As

is observed under moderate conditions between hexafluoroacetone and triphenyl arsine or triphenyl antimony. Krespan and Middleton[20] claimed that the unreactivity of triphenyl arsine is "perhaps as a result of lower stability of the cyclic products relative to those from triphenyl phosphine".

Similarly, phenylphosphorus perfluoropinacolate is more stable than its arsenic analogue. The phosphorus compound can be purified by distillation at 204 - 205° as reported by Conroy and Dresdner[35]. When same attempt is made to purify the phenylarsinic perfluoropinacolate, decomposition occurs at 150°.

Fluorine N. M. R. and Stereochemistry

The fluorine n. m. r. spectrum plays an important role in studying the stereochemistry of perfluoropinacol derivatives. One of these derivatives, the ortho-sulphite, has been investigated[34].



There are four possible ways in which the oxygen atoms in the molecule might be arranged about the sulphur atom, tetrahedral, square planar, trigonal bipyramidal or tetragonal pyramidal. The first two, however, are eliminated

by the appearance of the fluorine n. m. r. spectrum of the compound, which consists of two fairly broad absorptions of equal intensity at -10.5 and -12.2 p.p.m. from trifluoroacetic acid. This spectrum indicates the presence in the molecule of equal quantities of fluorine atoms in two different environments, which is in the case of bipyramidal or tetragonal pyramidal. However, only fluorine n. m. r. spectrum cannot distinguish the two.

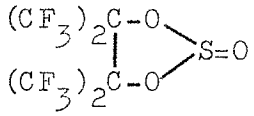
The fluorine n. m. r. spectra of triphenylphosphorus, triphenylarsenic and triphenylantimony perfluoropinacolates are, in each case, a singlet. This suggests that all the fluorine atoms are in the same magnetic environment. The following arrangements are possible for each compound, the P, As or Sb atom being at the center of the molecular geometry.

(1) trigonal bipyramid in which two oxygen atoms occupy two apices of the triangular plane,
(2) trigonal bipyramid in which one oxygen atom occupies one apex of the triangular plane and the other above (or below) the plane,
(3) square pyramidal, and
(4) equilibrium between (1) and (2) or (2) and (3) through pseudorotation.

However, in view of the common trigonal bipyramidal geometry of the Group V (V) compounds and the steric hindrance rendered by the large phenyl rings, (1) and (2) should be

more probable.

Two multiplets are observed in the fluorine n. m. r. spectrum of phenylarsenic perfluoropinacolate (Figure 2). It has the same fluorine n. m. r. spectral pattern with that of phenylphosphorus perfluoropinacolate[35] or the cyclic derivative of perfluoropinacol[54], which also shows two multiplets in the CF_3 region in each case.



These compounds, with the electron lone pairs residing on the heteroatoms (i.e. P, As or S), have the ligands in each case repelled out of the ring plane causing the fluorine atoms to be in different magnetic environments, six above and six below the plane of the five membered chelate ring, resulting in two multiplets.

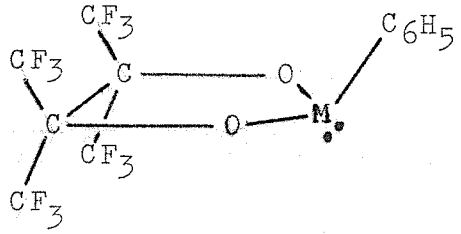
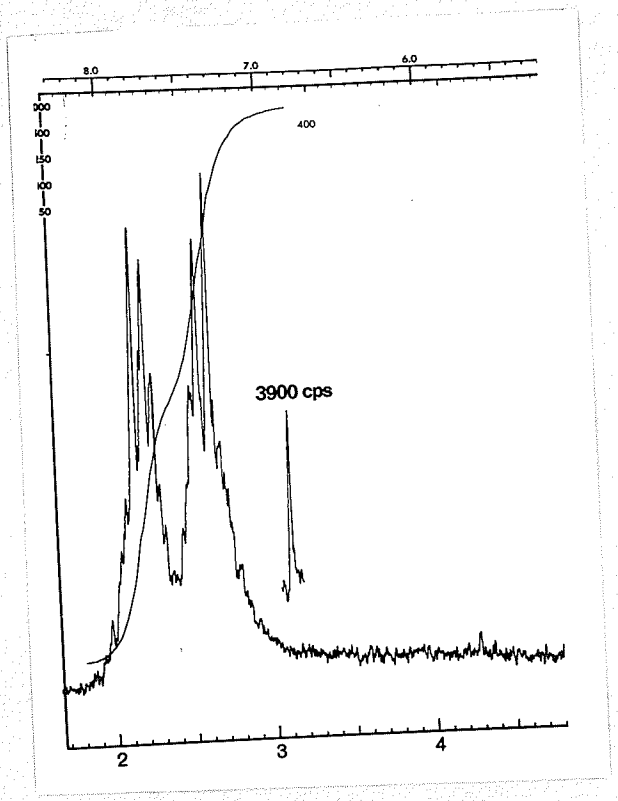


Figure 2

Fluorine N. M. R. Spectrum of Phenylarsenic Perfluoropinacolate



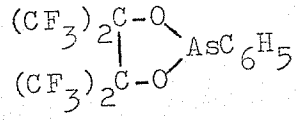


Table 3

Fluorine N. M. R. Peaks of Group V Perfluoropinacol Derivatives

Compounds	Solvent*	Peaks(p.p.m.)	Splitting
$(C_6H_5)_3P(PFP)$**	T.H.F.	68.17	Singlet
$(C_6H_5)_3As(PFP)$	Freon 11	67.85	Singlet
$(C_6H_5)_3Sb(PFP)$	Freon 11	68.89	Singlet
$C_6H_5P(PFP)^{35}$		65.40	Multiplet
		66.80	Multiplet
$C_6H_5As(PFP)$	Freon 11	67.15	Multiplet
		67.90	Multiplet

*T.H.F. stands for tetrahydrofuran,

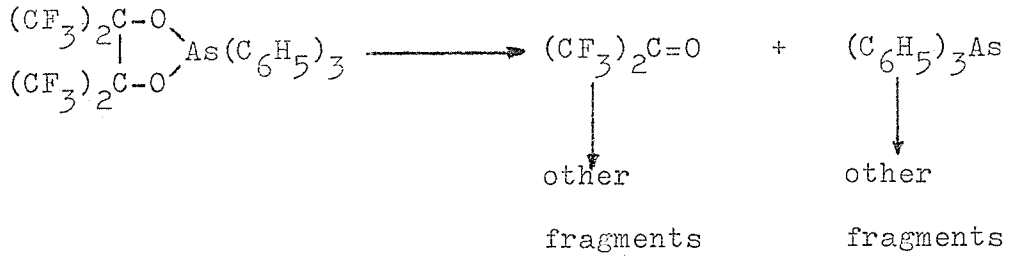
Freon 11 stands for trichlorofluoromethane.

**PFP stands for perfluoropinacolate, $-OC(CF_3)_2C(CF_3)_2O-$.

Mass Spectra

The more intense and important peaks of the mass spectra of triphenylphosphorus, triphenylarsenic and triphenylantimony perfluoropinacolates are tabulated in Tables 4, 5 and 6 respectively. The fragmentation patterns of triphenylphosphorus and triphenylantimony perfluoropinacolates are also shown in Figures 3 and 4.

The mass spectrum of triphenylarsenic perfluoropinacolate is interesting. There are apparently no peaks between the parent peak (638) and triphenyl arsine peak (316) and there is the appearance of the hexafluoroacetone peak (166). The other peaks can be assigned as the fragmentation particles from triphenyl arsine and hexafluoroacetone. Obviously, the decomposition mode of this compound is characterized by,



For the mass spectrum of triphenylantimony perfluoropinacolate, the appearance of very strong isotopic antimony peaks at 608 amd 610 is very characteristic. This fragment is assigned as (Parent - C_6H_4)$^+$ which does not exist in the mass spectrum of the phosphorus or arsine analogue of this family. The appearance of Sb-H group is certainly interesting.

Table 4

Mass Spectrum of Triphenylphosphorus Perfluoropinacolate

m/e	Relative Intenties	Assignment
575	1.4	$C_{24}H_{15}F_{11}PO_2^+$
525	3.1	$C_{23}H_{15}F_9PO_2^+$
517	4.0	$C_{18}H_{10}F_{12}PO_2^+$
379	3.1	$C_{16}H_{10}F_9PO_2^+$
262	22.3	$C_{18}H_{15}P^+$
201	13.1	$C_{12}H_{10}PO^+$
183	54.6	$C_{12}H_8P^+$
154	21.6	$C_{12}H_{10}^+$
152	10.8	$C_{12}H_8^+$
147	7.7	$C_3H_5O^+$
108	32.3	$C_6H_5P^+$
107	18.5	$C_6H_4P^+$
97	34.6	$C_2F_3O^+$
78	100.0	$C_6H_6^+$
77	36.9	$C_6H_5^+$
69	91.5	CF_3^+
52	24.6	$C_4H_4^+$
51	42.3	CHF_2^+ or $C_4H_3^+$
50	40.0	CF_2^+
39	20.8	$C_3H_3^+$
31	9.2	P^+ or CF^+

The relative intensity of the parent peak (594) is 0.1.

Figure 3

Mass Spectrum of Triphenylphosphorus Perfluoropinacolate

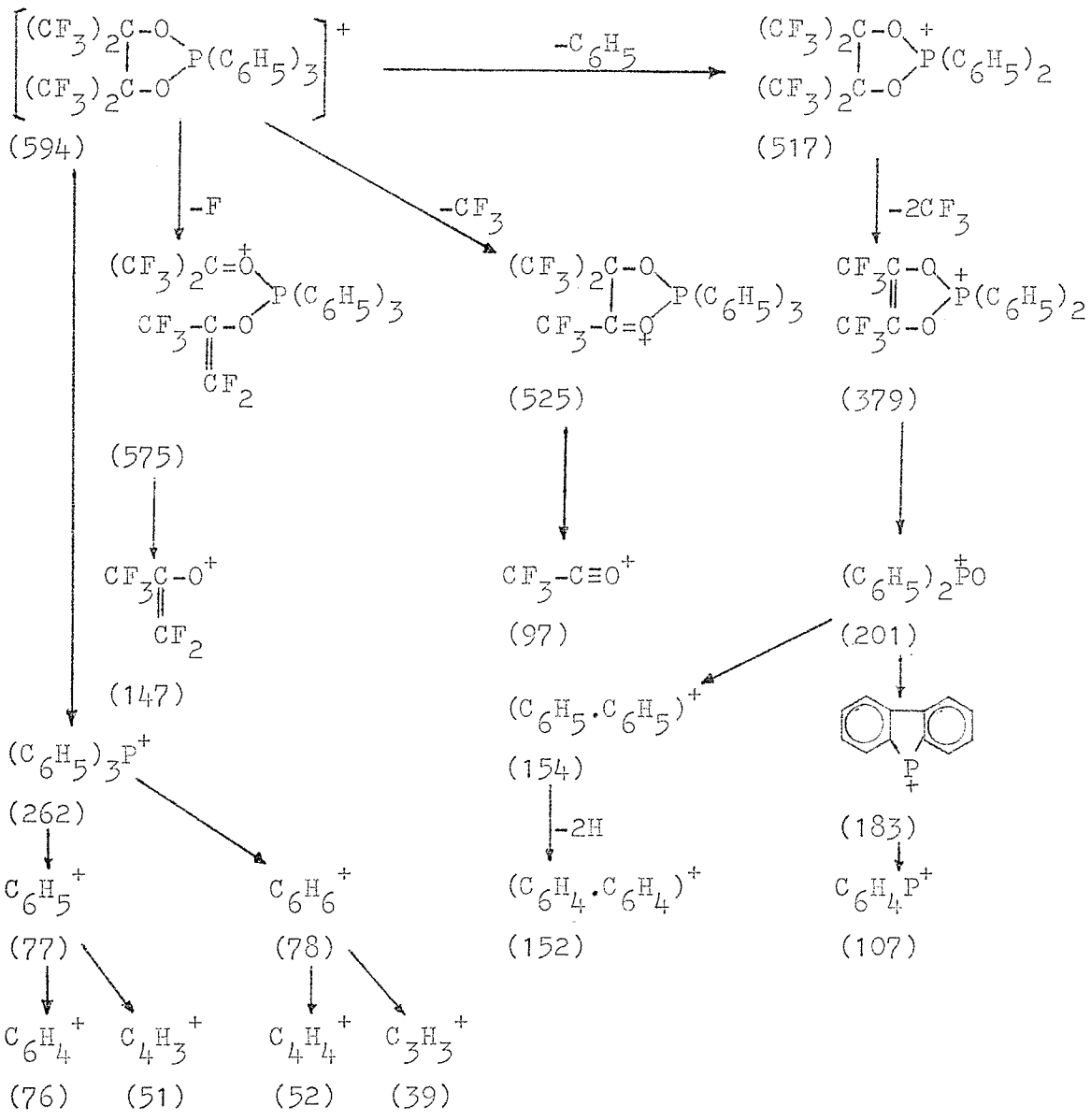


Table 5

Mass Spectrum of Triphenylarsenic Perfluoropinacolate

m/e	Relative Intensities	Assignment
306	1.5	$C_{18}H_{15}As^+$
229	0.5	$C_{12}H_{10}As^+$
227	1.4	$C_{12}H_8As^+$
166	0.2	$C_3F_6O^+$
154	0.5	$C_{12}H_{10}^+$
152	5.2	$C_6H_5As^+$
151	0.6	$C_6H_4As^+$
147	0.6	$C_3F_5O^+$
97	2.7	$C_2F_3O^+$
78	100.0	$C_6H_6^+$
77	2.7	$C_6H_5^+$
69	33.0	CF_3^+
52	1.6	$C_4H_4^+$
51	1.4	CHF_2^+ or $C_4H_3^+$
50	1.3	CF_2^+
39	0.9	$C_3H_3^+$

The relative intensity of the parent peak (638) is less than 0.01.

Table 6

Mass Spectrum of Triphenylantimony Perfluoropinacolate

m/e	Relative Intensities	Assignment
667	3.5	$C_{24}H_{15}F_{11}SbO_2^+$
665	4.5	
610	34.8	$C_{18}H_{11}F_{12}SbO_2^+$
608	42.1	
560	8.2	$C_{17}H_{11}F_{10}SbO_2^+$
558	10.4	
443	5.6	$C_{15}H_{10}F_6SbO^+$
441	6.2	
354	35.5	$C_{18}H_{15}Sb^+$
352	49.2	
277	11.3	$C_{12}H_{10}Sb^+$
275	17.1	
219	6.3	$C_6H_5FSb^+$
217	8.5	
200	63.1	$C_6H_5Sb^+$
198	84.6	
154	100.0	$C_{12}H_{10}^+$
153	15.6	$C_{12}H_9^+$

(Continued next page)

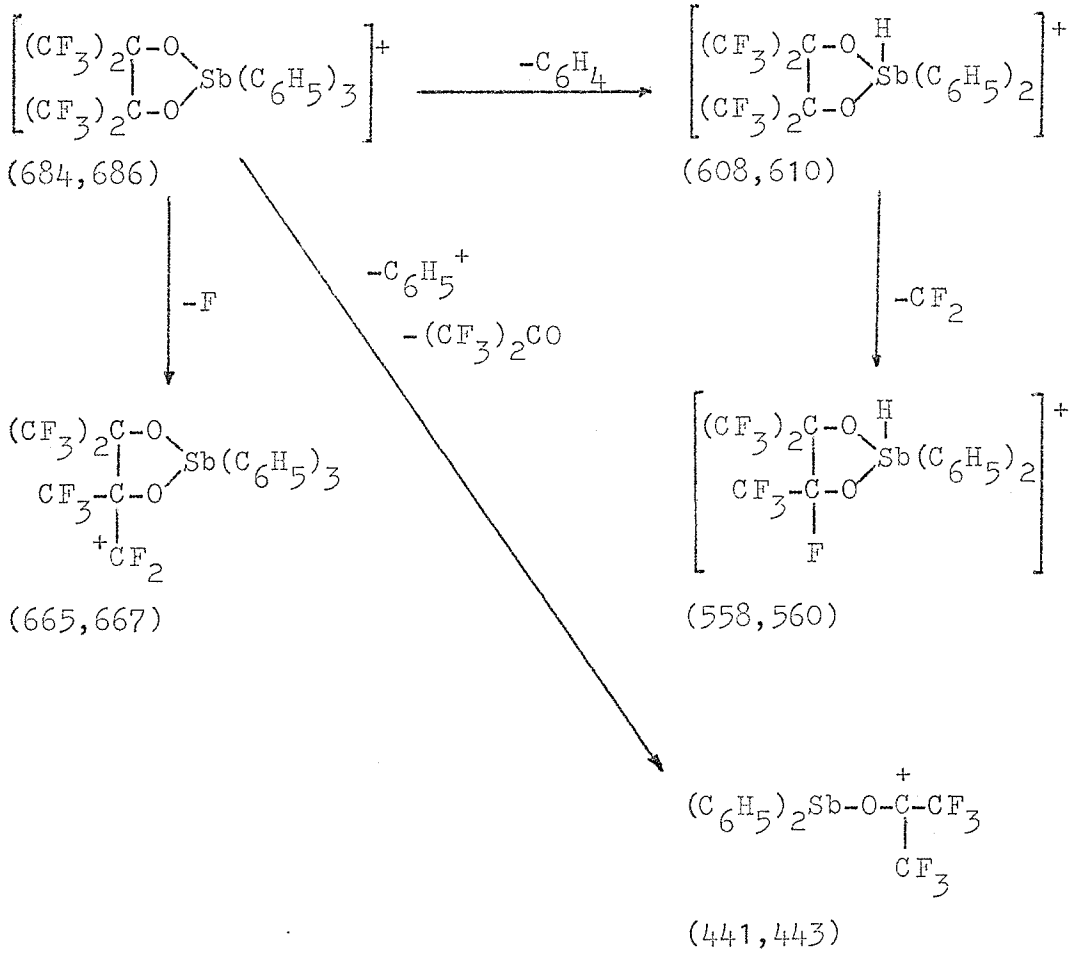
(Table 6 Continued)

152	11.8	$C_{12}H_8^+$
97	13.3	$C_2F_3O^+$
77	21.2	$C_6H_5^+$
69	20.8	CF_3^+
51	9.2	CHF_2^+ or $C_4H_3^+$

Two peaks are assigned to each antimony fragment due to the isotopes, ^{125}Sb and ^{123}Sb, the ratio of abundance being 3:4. The intensities of the parent peaks (686, 684) are 0.15 and 0.2 respectively. The following less intense antimony peaks are also found: $(C_6H_5)_2SbF_2^+$ (315, 313), $(C_6H_5)_2SbF^+$ (296, 294) and $C_6H_5SbF^+$ (219, 217).

Figure 4

Mass Spectrum of Triphenylantimony Perfluoropinacolate



From the fragmentation patterns of these three triphenyl Group V (V) perfluoropinacol derivatives, it is interesting to see that these compounds fragment in different ways, probably due to the different electronic nature of P(V), As(V) and Sb(V).

The more intense and important peaks of the mass spectra of phenylphosphorus and phenylarsenic perfluoropinacolates are tabulated in Tables 7 and 8 respectively. Their patterns of fragmentation are shown in Figures 5 and 6.

Complex Perfluoropinacolate Ions

Complex perfluoropinacolate anions have been prepared by the reaction of perfluoropinacol with a metal sulphate in water/methanol solution[57].

$$nH_2(PFP) + M^{n+} + 2nOH^- \longrightarrow (M(PFP)_n)^{n-} + 2nH_2O$$

1. M = Mn; n = 2
2. M = Fe; n = 3

(PFP stands for perfluoropinacolate, $-OC(CF_3)_2C(CF_3)_2O-$.)

When a solution of tetraphenyl arsenic chloride is added to disodium perfluoropinacolate, reaction occurs immediately and a white precipitate is formed. Extraction of this precipitate with acetonitrile yields a solution which shows a singlet at 71.26 p.p.m. in fluorine n. m. r.

Table 7

Mass Spectrum of Phenylphosphorus Perfluoropinacolate

(Recorded from A. P. Conroy & R. D. Dresdner, Inorg. Chem. 9, 2739 (1970).)

m/e	Relative Intensities	Assignment
440	3	$C_{12}F_{12}H_5PO_2^+$
421	55	$C_{12}F_{11}H_5PO_2^+$
371	6	$C_{11}F_9H_5PO_2^+$
143	> 100	$C_4F_5^+$
127	57	$C_6H_5FP^+$
108	28	$C_6H_5P^+$
107	61	$C_6H_4P^+$
77	100	$C_6H_5^+$
69	69	CF_3^+
50	70	CF_2^+
47	15	PO^+

Figure 5

Mass Spectrum of Phenylphosphorus Perfluoropinacolate

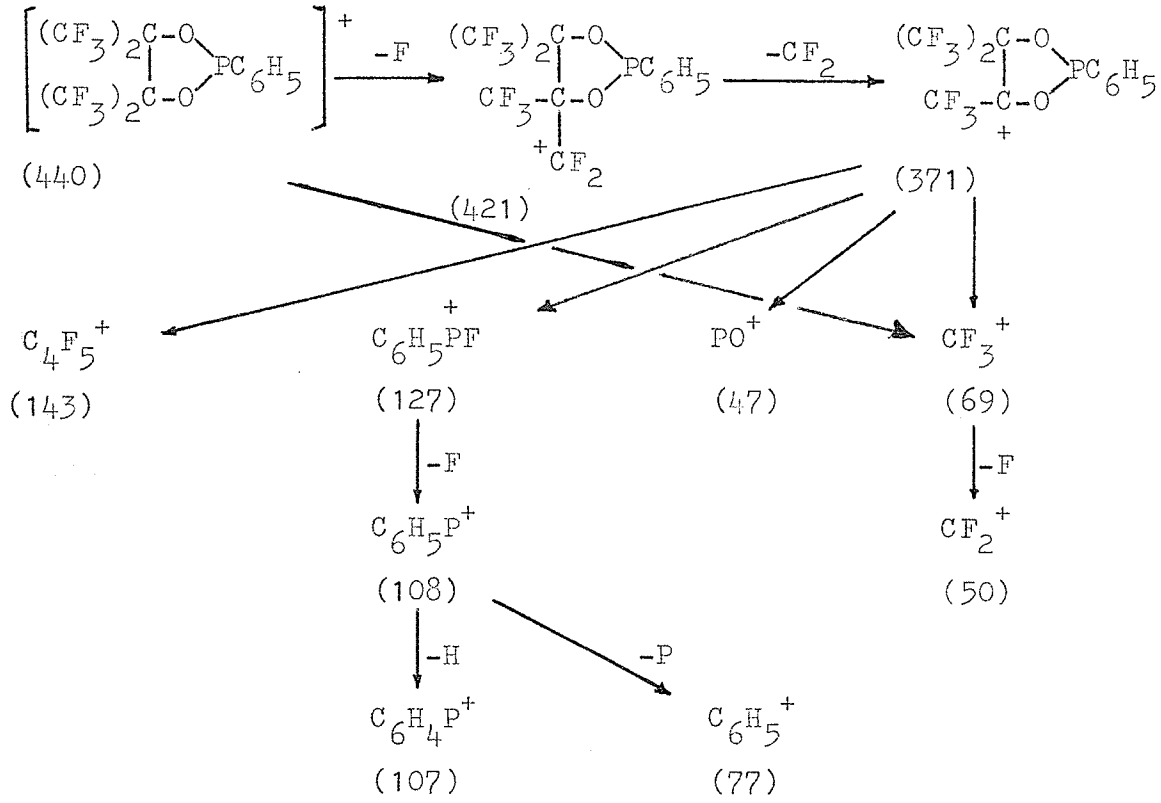


Table 8

Mass Spectrum of Phenylarsenic Perfluoropinacolate

m/e	Relative Intensities	Assignment
240	6.7	$C_7H_5F_4As^+$
229	4.3	$C_3F_7AsO^+$
171	48.7	$C_6H_5FAs^+$
167	18.7	$C_6H_4AsO^+$
152	100.0	$C_6H_5As^+$
151	4.0	$C_6H_4As^+$
139	7.3	$C_5H_4As^+$
113	6.0	F_2As^+
112	10.7	$C_3F_4^+$
100	11.3	$C_2F_4^+$
97	4.7	$C_2F_3O^+$
91	5.3	AsO^+
78	7.3	$C_2F_2O^+$
77	93.4	$C_6H_5^+$
75	8.0	As^+
69	40.0	CF_3^+
51	6.7	CHF_2^+ or $C_4H_3^+$
50	20.0	CF_2^+
39	10.7	$C_3H_3^+$

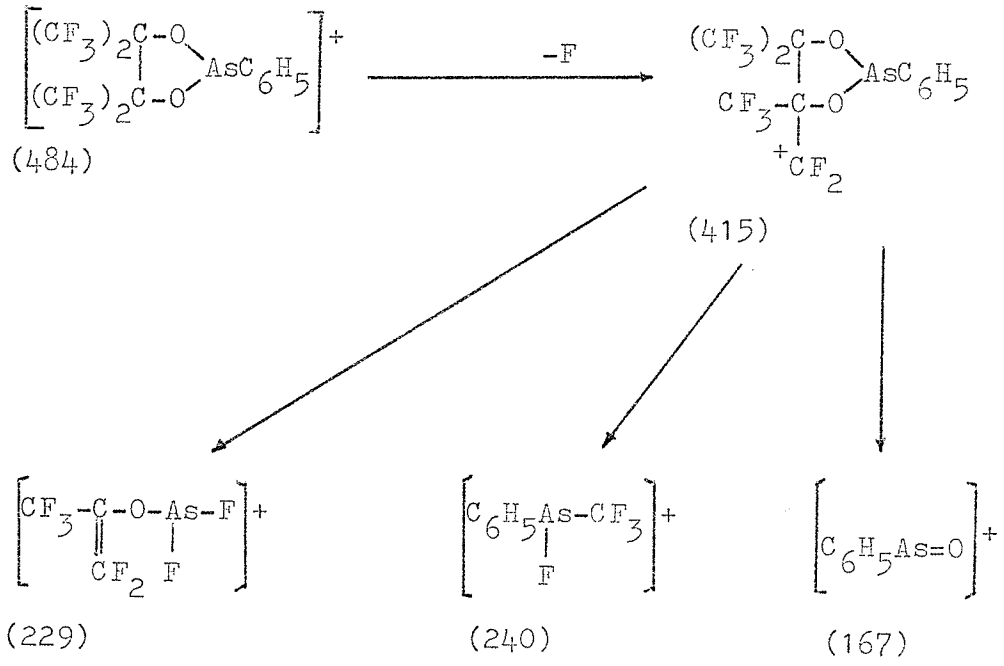
(Continued next page)

(Table 8 Continued)

The C_6H_5AsCl peaks at 187,189 (relative intensities 10,4) and $C_6H_5AsCl_2$ peaks at 222,224 (relative intensities less than 5) are present due to the impurity phenyl arsenic dichloride. The parent peak (484) has an intensity 0.8 and the (Parent - F) peak (415) has an intensity 0.7.

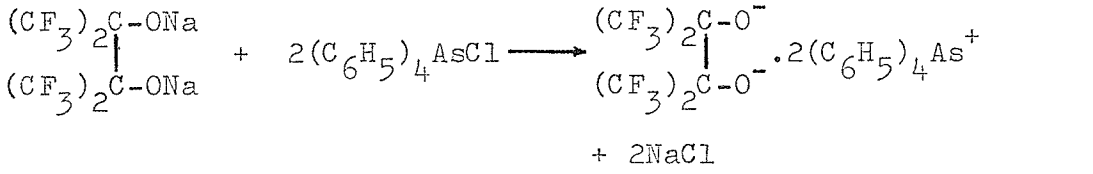
Figure 6

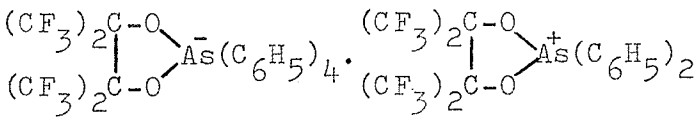
Mass Spectrum of Phenylarsenic Perfluoropinacolate



spectrum. The infrared spectrum, taken after most of the solvent has evaporated away, shows the presence of strong C-F absorption but the absence of the characteristic absorption of the five-membered ring.

Based on these spectral data, the following reaction can be suggested.



The possibility of the formation of a double ions of perfluoropinacolate,  is eliminated since in this case, two singlets should be observed.

Attempts to isolate the salt in aqueous solution was not successful. When another attempts were made to recrystallize the compound in ether, the end product was triphenyl arsenic oxide.

PART 3 Fluorinated Alchols

Perfluoropinacol, also known as dodecafluoropinacol, was firstly prepared through the photochemical irradiation of hexafluoroacetone and isopropyl alcohol[43].

$$(CF_3)_2CO + (CH_3)_2COH \xrightarrow{U.V.} HOC(CF_3)_2C(CF_3)_2OH$$

It has also been prepared via a triethyl phosphite intermediate. The latter was formed in high yield merely on mixing the two reagents[24].

$$(CF_3)_2CO + (C_2H_5O)_3P \longrightarrow \begin{matrix}(CF_3)_2C\text{-}O \\ | \quad\quad P(OC_2H_5)_3 \\ (CF_3)_2C\text{-}O\end{matrix}$$

Saponification of the cyclic phosphorane to an acid followed by prolonged heating of the acid produced perfluoropinacol. Reaction of hexafluoroacetone with triphenyl phosphine has also been reported to give a phospholane, which on hydrolysis liberated perfluoropinacol[26].

A mass spectrum of the perfluoropinacol was obtained. Its important peaks are listed in Table 9 and the fragmentation pattern is shown in Figure 7.

The appearance of the $(CF_3)_2\overset{+}{C}OH$ species (167) is very

Table 9

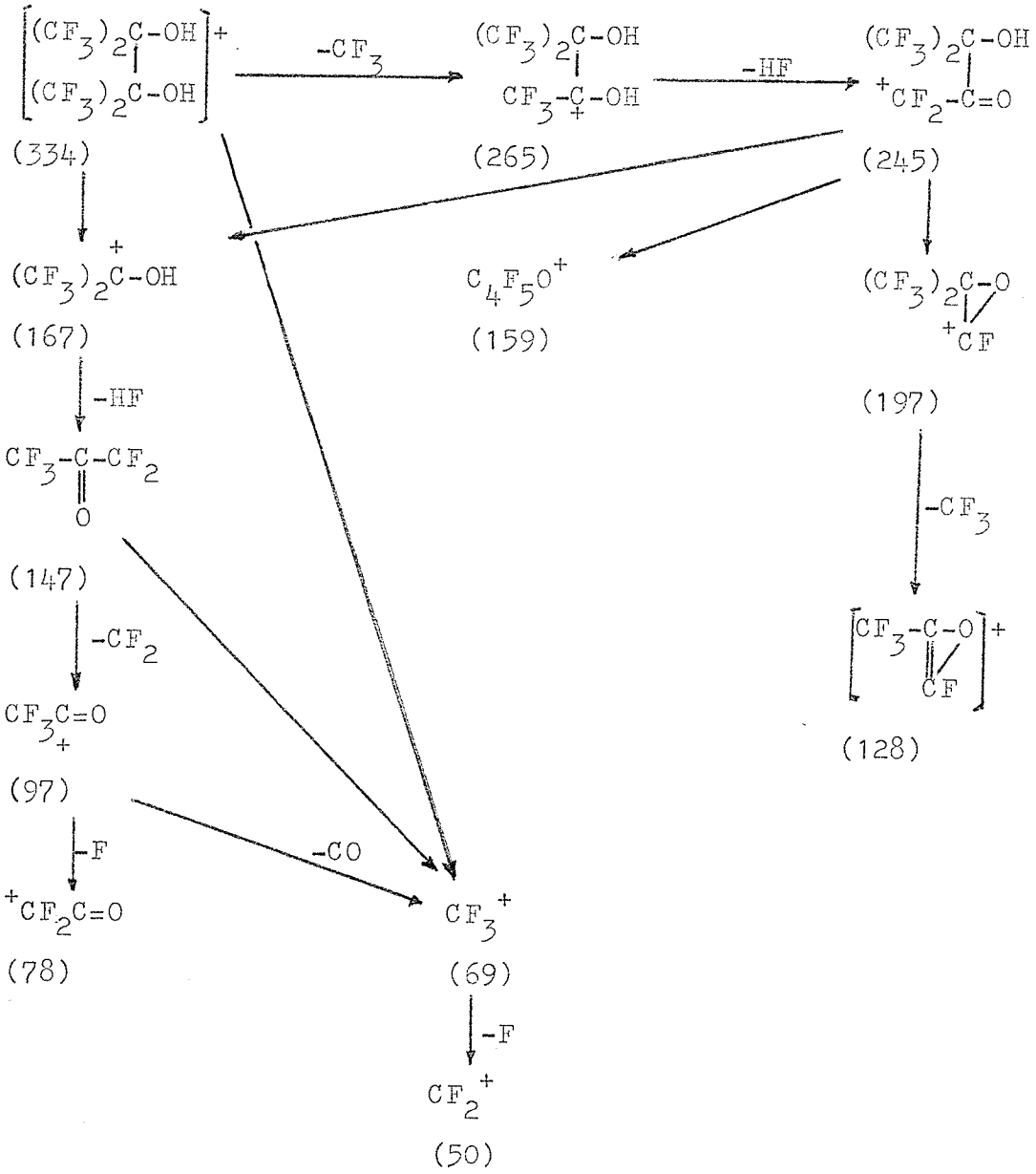
Mass Spectrum of Perfluoropinacol

m/e	Relative Intensities	Assignment
265	1.7	$C_5H_2F_9O_2^+$
245	2.2	$C_5HF_8O_2^+$
197	2.6	$C_4F_7O^+$
167	10.3	$C_3HF_6O^+$
159	3.9	$C_4F_5O^+$
147	26.3	$C_2F_5O^+$
128	12.5	$C_3F_4O^+$
97	35.5	$C_2F_3O^+$
78	12.9	$C_2F_2O^+$
69	100.0	CF_3^+
51	14.5	CHF_2^+
50	10.8	CF_2^+

The relative intensity of the parent peak (334) is less than 0.1.

Figure 7

Mass Spectrum of Perfluoropinacol



characteristic. It is believed to be formed from the fission of the parent perfluoropinacol into two equal fragments.

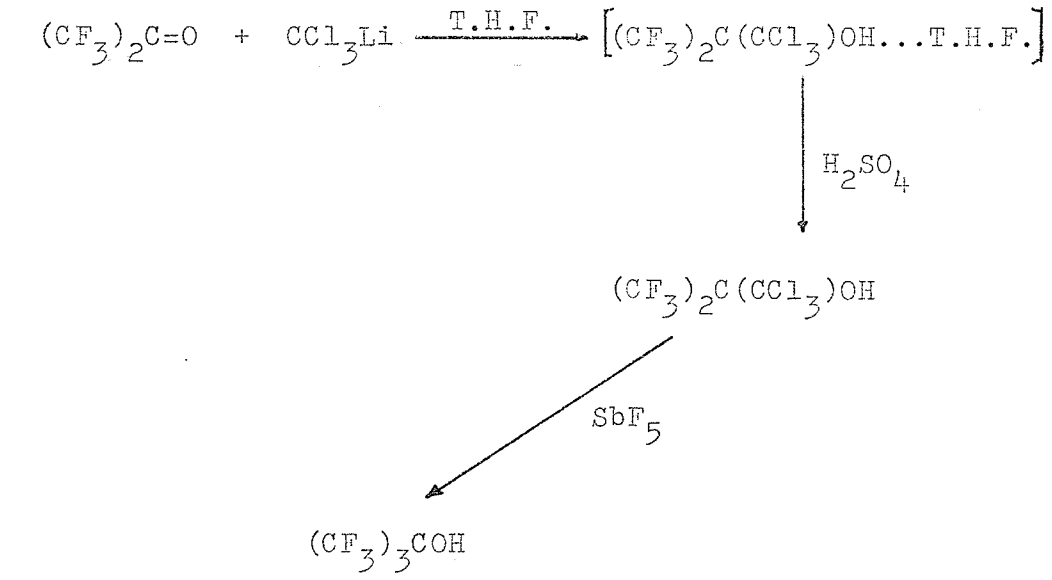
$$\left[\begin{matrix}(CF_3)_2C\text{-}OH \\ | \\ (CF_3)_2C\text{-}OH\end{matrix}\right]^+ \longrightarrow (CF_3)_2\overset{+}{C}\text{-}OH \quad + \quad (CF_3)_2\overset{\cdot}{C}\text{-}OH$$

This fission is very interesting since in the preparation of perfluoropinacol from hexafluoroacetone and isopropyl alcohol[43], perfluoropinacol is formed from the dimerization of the $(CF_3)_2\overset{\cdot}{C}OH$ radical.

$$2(CF_3)_2\overset{\cdot}{C}OH \longrightarrow \begin{matrix}(CF_3)_2C\text{-}OH \\ | \\ (CF_3)_2C\text{-}OH\end{matrix}$$

Perfluoro-t-butyl alcohol, $(CF_3)_3COH$, has been the subject of controversy with regard to its method of preparation. Knunyants[47] was the first one who synthesized and isolated this alcohol involving the oxidation of $(CF_3)_3CNO$ to $(CF_3)_3CONO$ and hydrolysis of the nitrile.

Filler and Schure[48] synthesized this compound by the more direct method, the reaction of trichloromethyl-lithium with hexafluoroacetone, which gave $(CF_3)_2C(CCl_3)OH$ as an intermediate.



A much more direct method was attempted to prepare the perfluoro-t-butyl alcohol via the memtioned intermediate. When neat samples of chloroform and hexafluoroacetone were irradiated with ultra violet light, a product with the following spectroscopic properties was obtained in low yield.

Infrared:	3570 cm^{-1}
Proton n.m.r.:	6.04 τ
Fluorine n.m.r.:	67.45 p.p.m. (singlet)

Filler and Schure[48] reported that the O-H infrared absorption and the proton n. m. r. value of $(CF_3)_2C(CCl_3)OH$ are at 3570 cm^{-1} and 6.04 τ respectively. Based on these consistencies and the fluorine n. m. r. data, the formation of $(CF_3)_2C(CCl_3)OH$ from the reaction of chloroform and hexafluoroacetone can be suggested.

However, when the photochemical reaction of chloroform and hexafluoroacetone took place with tetrahydrofuran as the solvent, perfluoropinacol (yield about 15 %) and another product (yield about 6 %) were obtained. The spectroscopic properties of the new product are,

Proton n.m.r.:	5.63 τ (septet)	(J = 6 cps)
Fluorine n.m.r.:	76.00 p.p.m.(doublet)	(J = 6 cps)

The spectroscopic properties of the new product are consistent with the $(CF_3)_2CHOH$ which was isolated by Middleton and Lindsey[43].

However, both compounds were not isolated or further characterised. Based on the assumption of their existence through spectroscopic evidence, a reaction mechanism can be rationalized.

In the absence of a solvent:

$$CHCl_3 \xrightarrow{U.V.} .H + .CCl_3$$

$$(CF_3)_2C{=}O + .H \longrightarrow (CF_3)_2\overset{\cdot}{C}\text{-}OH$$

$$(CF_3)_2\overset{\cdot}{C}\text{-}OH + .CCl_3 \longrightarrow (CF_3)_2C(CCl_3)\text{-}OH$$

In the presence of a solvent, tetrahydrofuran, the reactivity of the $\cdot CCl_3$ radicals is probably hindered by the solvent by some unknown mechanism. The other alcohols are produced.

$$(CF_3)_2\overset{\cdot}{C}\text{-}OH + .H \longrightarrow (CF_3)_2C(H)\text{-}OH$$

$$2\ (CF_3)_2\overset{\cdot}{C}\text{-}OH \longrightarrow (CF_3)_2C(OH)\text{-}C(CF_3)_2\text{-}OH$$

The formation of $(CF_3)_2\overset{\cdot}{C}\text{-}OH$ and its dimerization to form the perfluoropinacol have been described by Middleton and Lindsey[43].

When neat samples of pentafluorochloroacetone and chloroform were irradiated with ultra violet light, a product with the following spectroscopic properties was obtained in low yield.

Infrared: 3570 cm^{-1}

Proton n. m. r.: 6.18 τ

Fluorine n.m.r.: 73.20 p.p.m.(triplet) (J = 8 cps.)

66.00 p.p.m.(doublet) (J = 8 cps.)

Since its infrared absorption is at exactly the same position as the O-H absorption of $(CF_3)_2C(CCl_3)OH$[48], very probably a similar compound $CF_3C(CF_2Cl)(CCl_3)OH$ was formed. However, the possibility of the formation of a di-alcohol, $CF_3C(CF_2Cl)OH$, cannot be eliminated.

$CF_3C(CF_2Cl)OH$

When tetrahydrofuran was added as a solvent to the photochemical reaction of pentafluorochloroacetone and chloroform, the products formed were quite complicated. The fluorine n. m. r. spectrum shows a number of doublets of triplets and other peaks. The products are believed to contain various groups of CF_3-CH-[50] which are believed to arise from the radical reaction. Since no O-H absorption is detected in both the proton n. m. r. and infrared spectra, no further investigation was made.

CF_2Cl

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